VCCTL: A Web-Based Virtual Cement and Concrete Testing Laboratory

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Vision of VCCTL

- Can you imagine designing a complicated, expensive building empirically, without the use of finite element computational tools?
- …yet we design concrete materials empirically
- **VISION:** ***Computer-design construction materials just like engineers computer-design structures***

What is NIST?

- NIST = National Institute of Standards and Technology
- Department of Commerce laboratory
- 100 years of doing basic measurement technology research for the aid of scientifically-based industrial standardization
- Cement research at NIST began in 1917
- Long history of cooperation between PCA and NIST, since the 1920's (Bogue and Blaine)

NIST: The HYPERCON Program

Bringing basic experimental and computational materials science tools to bear on the prediction and optimization of real-world concrete properties

- **Tool 1**: *High-tech materials science experiments* including scanning electron microscopy; X-ray diffraction, absorption, and tomography; rheometry; and ion chromatography
- **Tool 2**: *World-leading advanced computational materials science*, using parallel processing, to predict concrete microstructure and properties
- **Main output**: Collaboration with industry in the Virtual Cement and Concrete Testing Laboratory

Why Develop a Virtual Testing Lab?

- Current testing
  - physical based
  - manpower intensive
  - materials intensive
  - weeks/months
  - high disposal costs
- Virtual testing
  - computer based
  - computation intensive
  - small material needs
  - days
  - low disposal costs

But characterization is the key

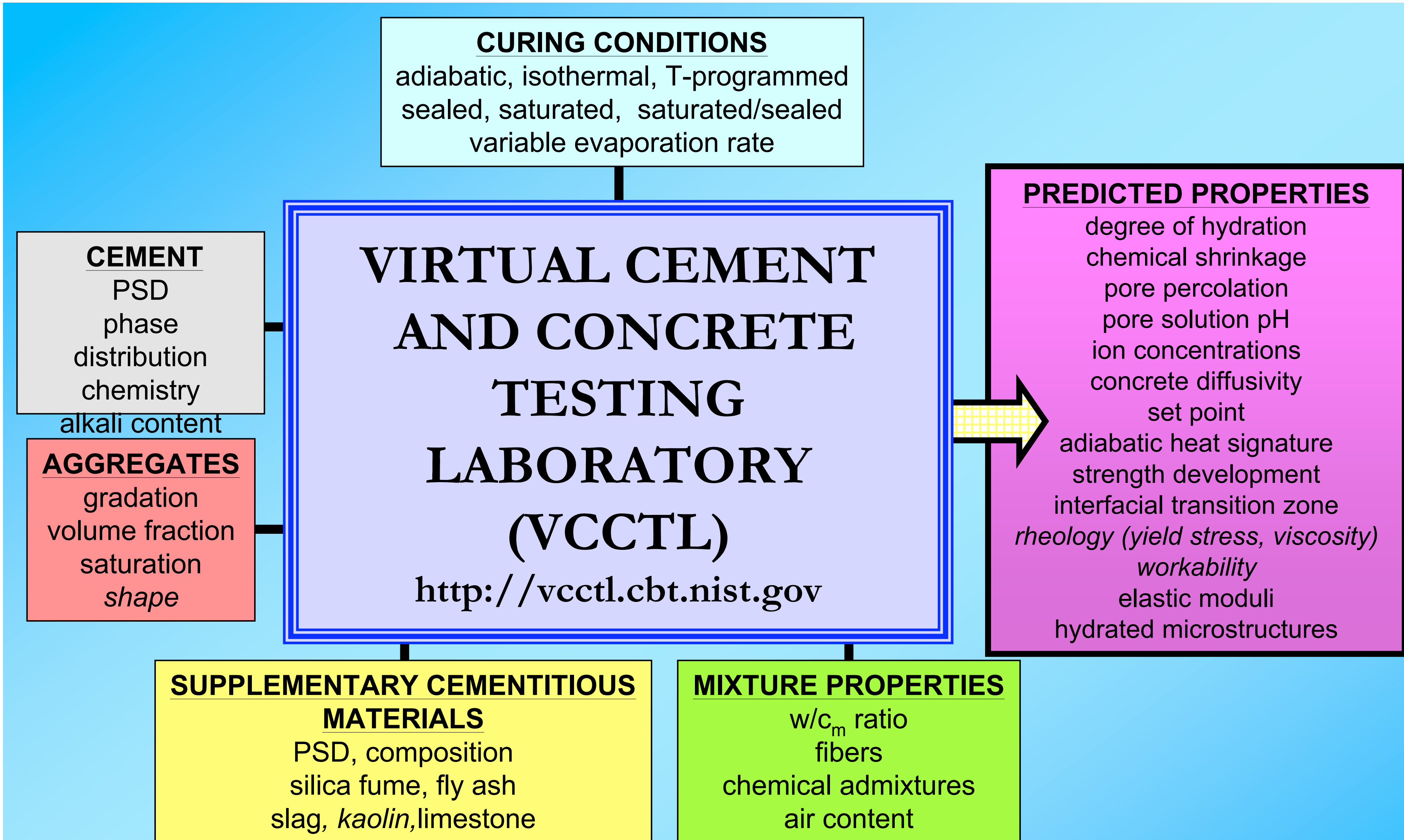
- To enable virtual testing requires characterization of raw materials (cement, aggregates, mineral admixtures) far beyond what has been systematically done before
- BUT: will enable modeling to be used profitably

What Is The Virtual Cement and Concrete Testing Laboratory?

- Internet-based and menu driven
- Predicts properties based on detailed microstructure simulations of well-characterized starting materials
- Goal is to reduce number of physical concrete tests, thus expediting the R&D process and enabling optimization in the material design process

History of the research behind the VCCTL

- 1982 – Development at NIST, under Geoff Frohnsdorff's leadership, by Hamlin Jennings of first simple cement hydration model (continuum based)
- 1989
  - NIST starts developing first (primitive) pixel-based simulation of cement hydration
  - NIST starts developing finite difference methods for computing properties of pixel-based systems
- January 1, 2001 – Start of VCCTL
- So VCCTL is organization and further development, for industry benefit, of ~20 years of NIST research
  - Collaboration between three NIST laboratories – Building and Fire Research, Information Technology, and Materials Science and Engineering



Industrial Participants

CEMEX, Dyckerhoff Zement GmbH, HOLCIM INC., International Center for Aggregate Research, Master Builders Technologies, PCA, Verein Deutscher Zementwerke e.V., W.R. Grace & Co.- CT

VCCTL Consortium:
Industry Relevance and Leveraging

- Eight companies at present (Cemex, Holcim, Portland Cement Association, W.R. Grace, Master Builders, Dyckerhoff, VDZ, ICAR) at $40K/year plus research collaboration
- Well over 100% match by NIST funds
- All generic concrete raw material groups are represented in VCCTL – cement (portland and blended), chemical admixtures, and aggregates

VCCTL Interface

- Web-based
  - http://vcctl.cbt.nist.gov (Version 1.0)
  - advanced versions at member sites
  - Javascript, Perl, and cgi code to accept and validate user inputs and return results
  - Gnuplot to create graphs of model (and experimental) results
- Interface launches to C modeling engines

VCCTL Web Interface

Inputs for Slag Characteristics

Property	Slag	Slag hydration product
Molecular mass (g/mol)	2492.4	4307.085
Specific gravity (g/cm^3)	2.87	2.35
Molar volume (cm^3/mol)– calculated	868.43	1832.802
Ca/Si molar ratio	0.97	1.25
Si per mole of slag	17.0	---
H2O/Si molar ratio	---	5.059

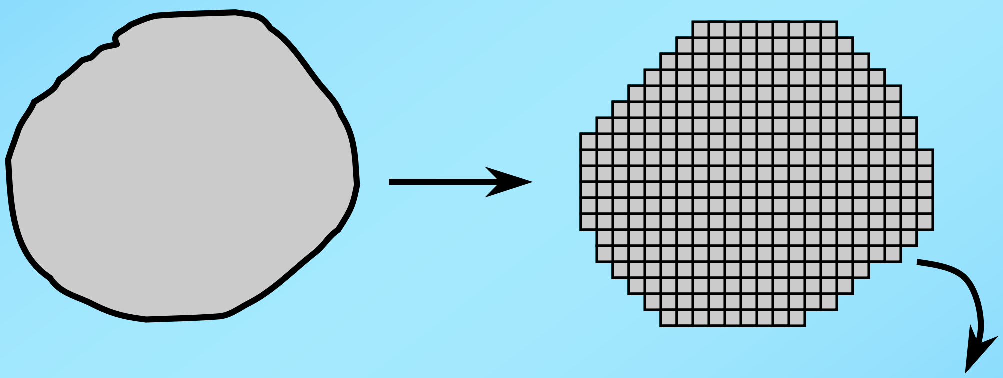
Filename to be created: slagone.dat

Submit form to store slag characteristics

Return to the main menu

Modeling Approach

- Microstructure-Based
  - Spatial resolution at the sub-particle level using small volume elements (1 μm^3)



Each volume element has properties of the phase at that location in space

What Input is Needed for Microstructure-Based Models?

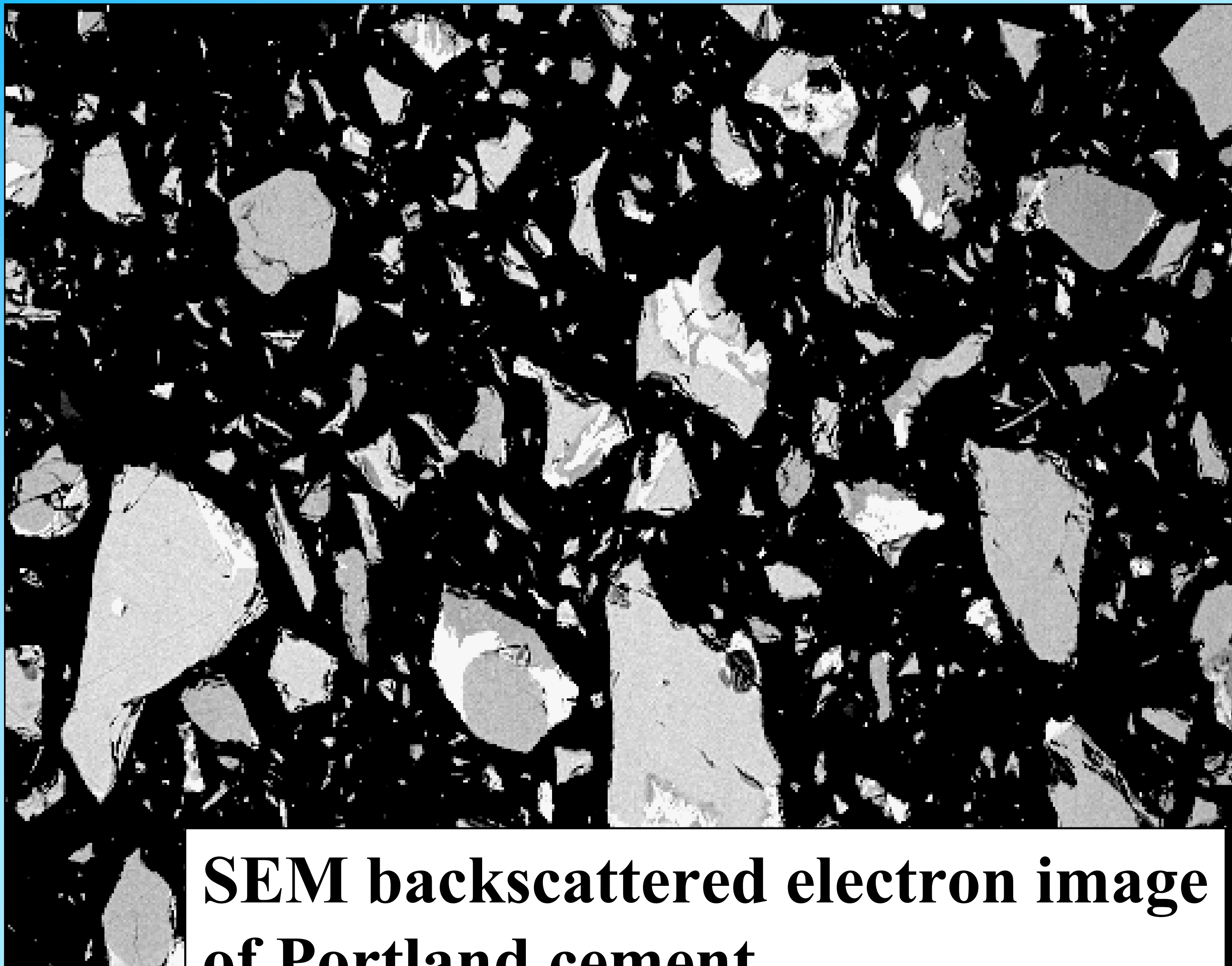
- Individual Phase Properties
  - Specific heat, heat of formation, elastic moduli, etc.
- Microstructure Information
  - Cement (mineral admixture) particle size distribution
  - Cement phase composition and distribution
  - Gypsum content and form (hemihydrate, anhydrite)
  - Flocculation/Dispersion
  - Volume fraction of aggregates
- Kinetic Information
  - Model reaction mechanisms
  - Activation energies (cement and admixtures)
  - Curing conditions (isothermal/adiabatic, saturated/sealed)

What Kind of Problems Can the VCCTL Address?

- 3-D microstructures
- Degree of hydration of all phases
  - phase fractions vs. time
- Heat release
  - adiabatic heat signature
- Chemical shrinkage
- Compressive strength (via Power's gel-space ratio)
- Elastic moduli
- Phase percolation properties (set point and capillary porosity)
- Diffusivity coefficient predictions (conductivities)
- Pore solution pH, ionic concentrations, and conductivity

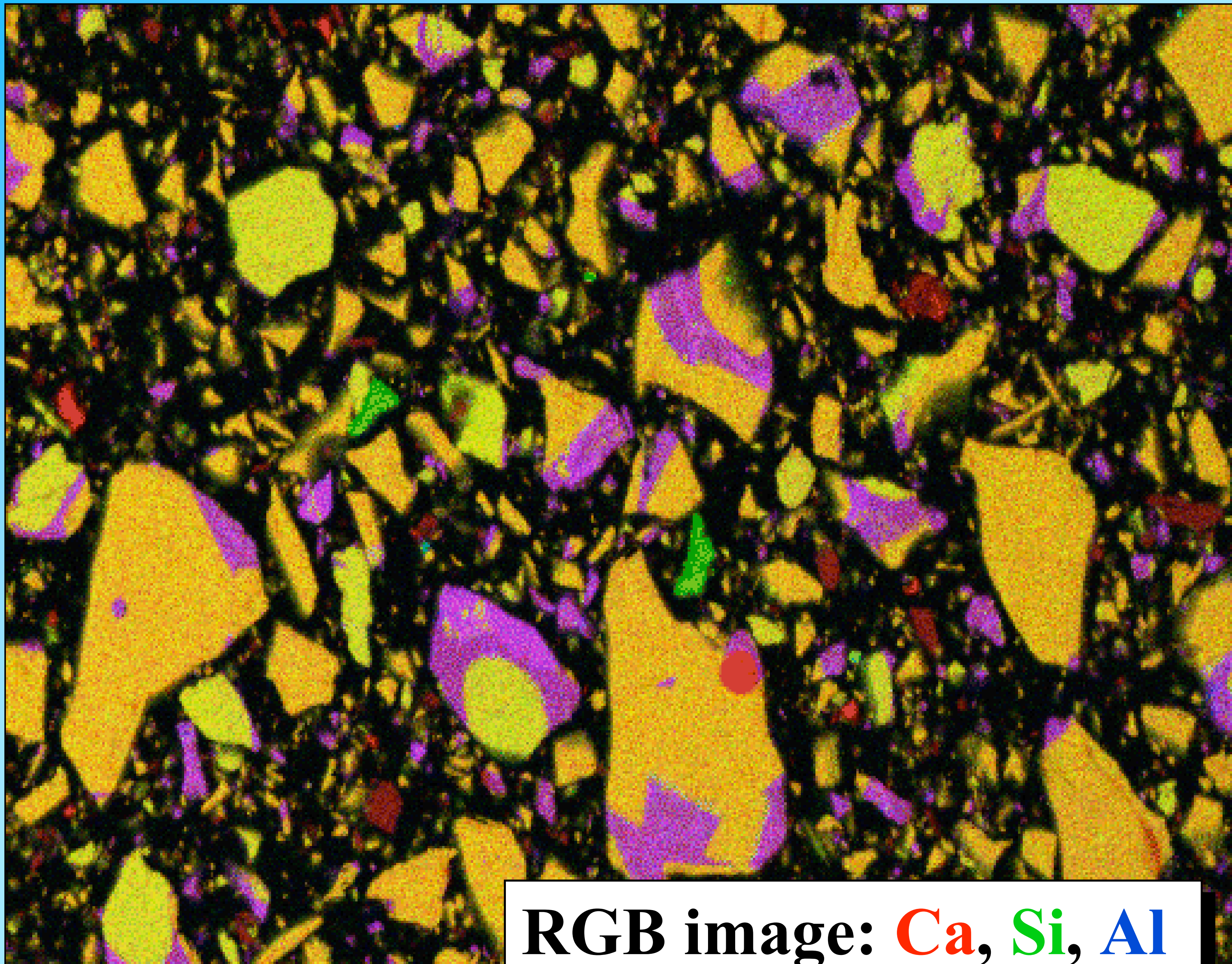
How to Obtain Microstructure Input Data?

Characterize Real Cement Microstructures!



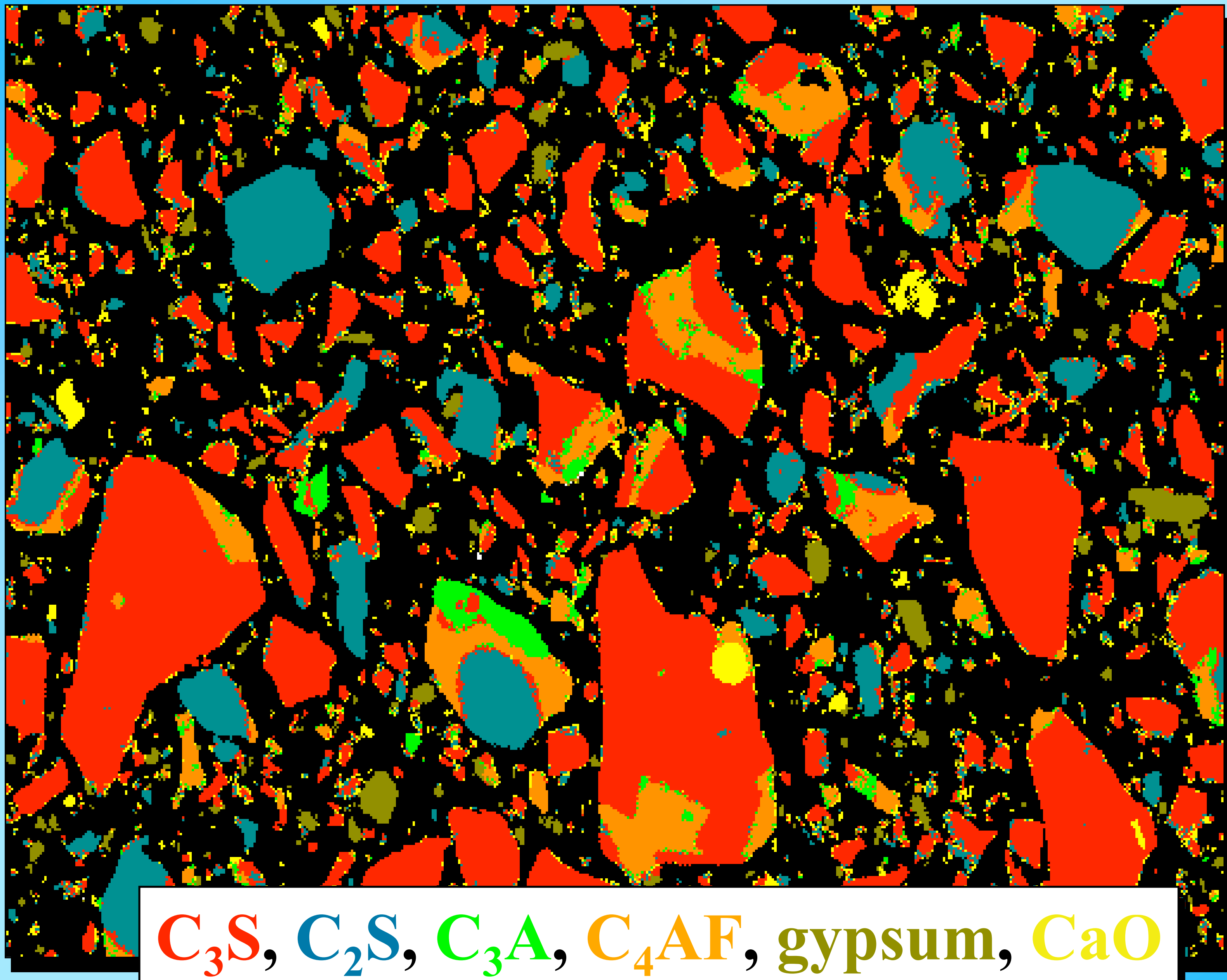
SEM backscattered electron image of Portland cement

(courtesy of Paul Stutzman)

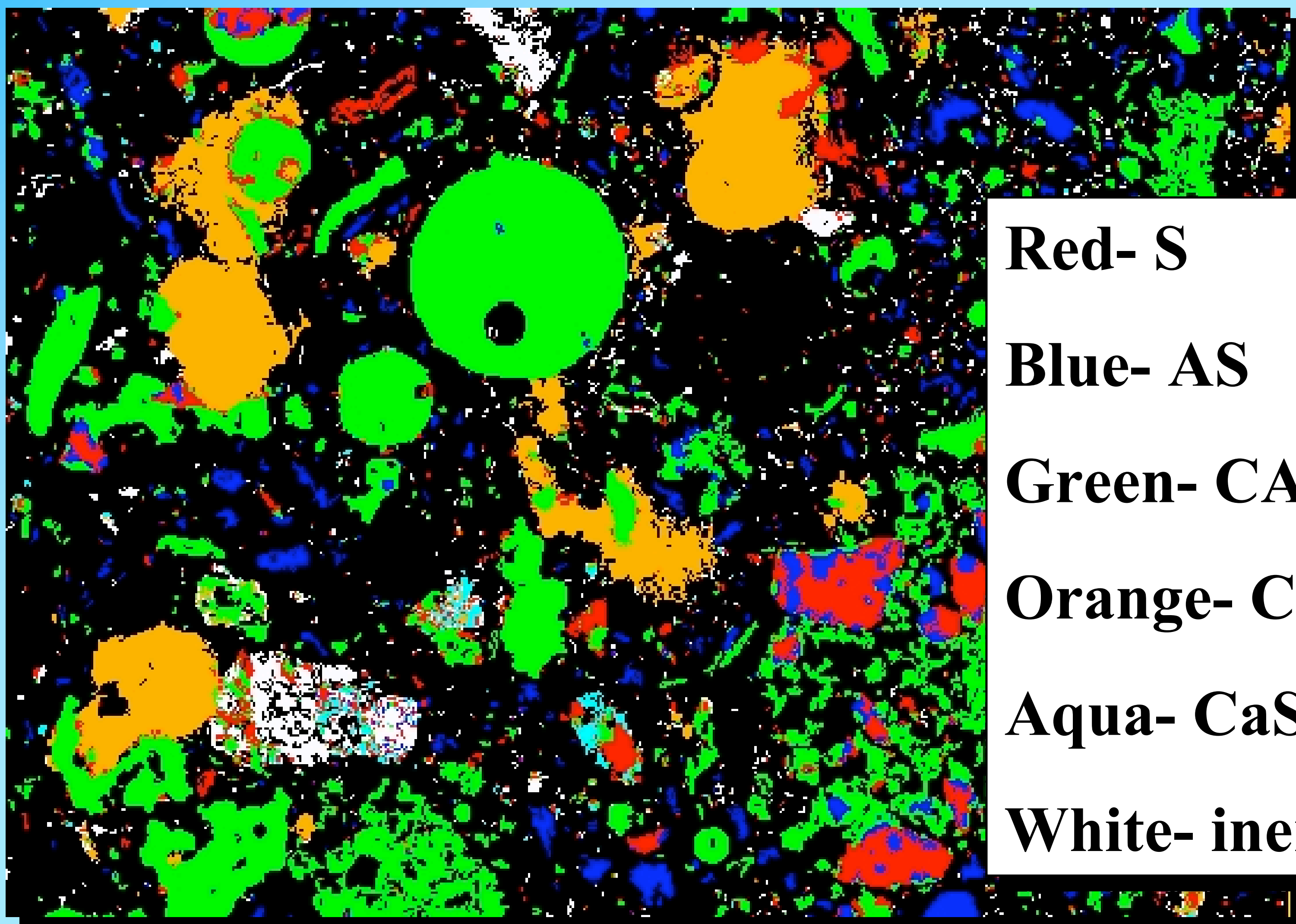


RGB image: Ca, Si, Al

(courtesty of Paul Stutzman)


C_3S, C_2S, C_3A, C_4AF, gypsum, CaO

SEM/X-ray Characterization of Fly Ash (Municipal Waste Fly Ash from France)



Red- S

Blue- AS

Green- CAS_2

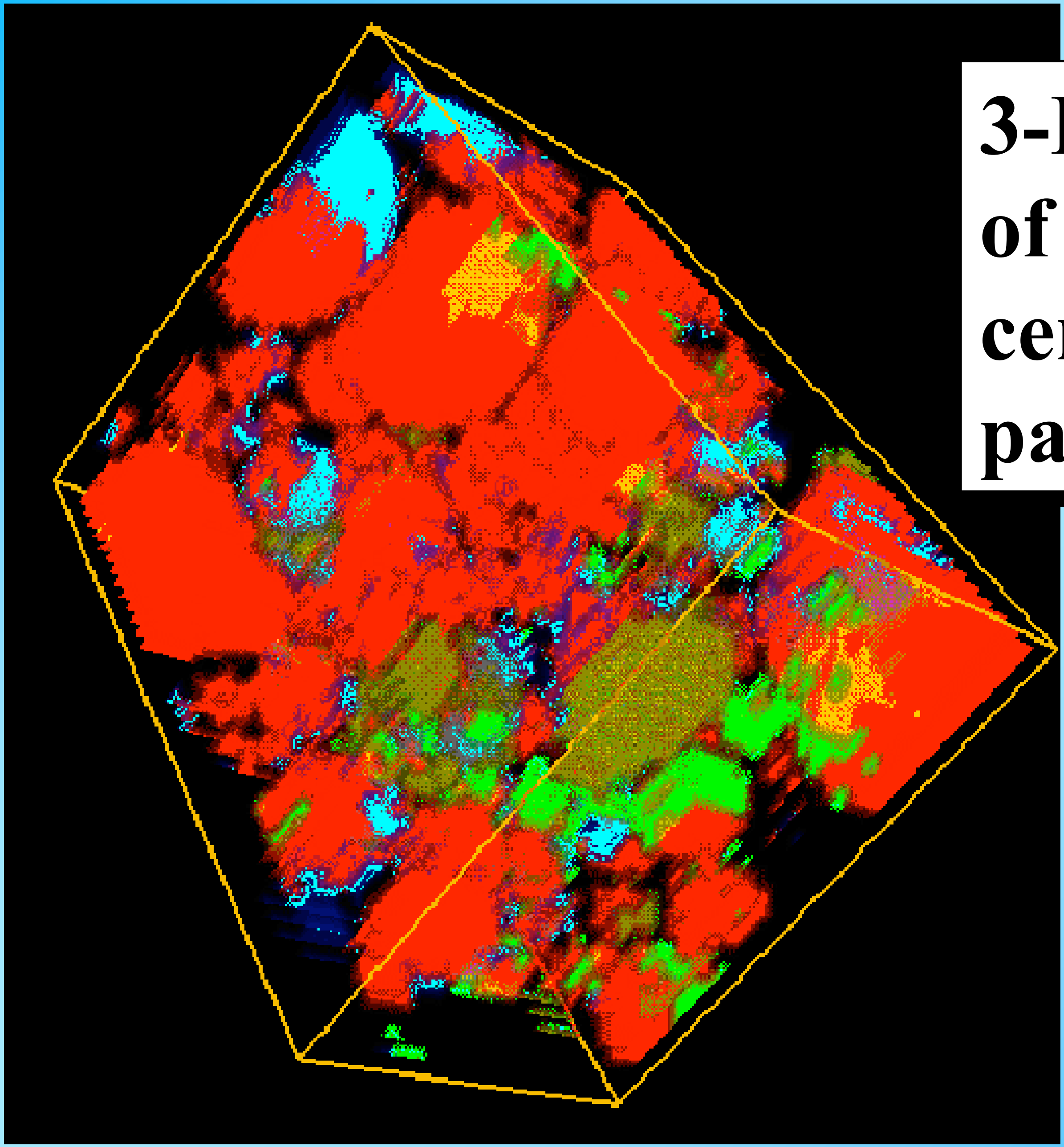
Orange- $CaCl_2$

Aqua- $CaSO_4$

White- inert

How Can We Construct 3-D Microstructures from 2-D Images?

- Autocorrelation functions
  - provide information on volume fraction and surface area fraction of individual phases
  - are identical in 2-D and 3-D!
- Measure autocorrelation functions on 2-D images for each clinker phase
- Use them to build a 3-D microstructure that is consistent with these functions



3-D image of model cement particles

Cement Image & PSD Database

- Internet accessible database at http://ciks.cbt.nist.gov/phpct/database/images
- Contains processed image, particle size distribution (PSD), and phase composition for each cement (links to ftp site to download correlation and related files)
- Version 1.0 contains data for 26 cements from 7 countries
- Versions at member sites can be customized for IP purposes

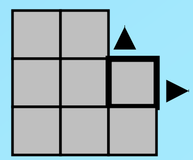
VCCTL:
Better Understanding ⇔ Improved Models

- Extension of hydration model
  - alkali species (pore solution composition) influence on hydration kinetics (NIST, Cemex, Dyckerhoff, W.R. Grace, VDZ)
  - realistic cement particle shapes (NIST)
  - more accurate modeling of slag hydration (NIST, Dyckerhoff)
- Standardization of PSD measurement (All, ASTM)
- Rheological properties (yield stress and viscosity)
  - interactions between air entrainment and rheology (NIST, Grace, and Master Builders)
- Elastic and visco-elastic properties
  - model validation (NIST, Dyckerhoff, Holcim)
- Aggregate shape effects on concrete properties (NIST, ICAR, all)

Module for
Cement Paste Hydration

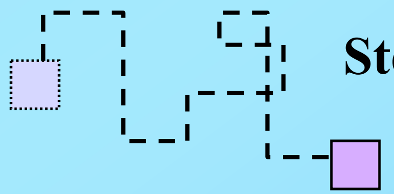
How is Hydration Modeled?

- Cellular automaton approach
  - Each volume element is an independent agent that can
    - **Dissolve**



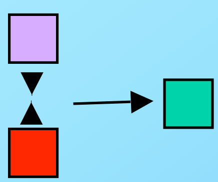
Pore solution

- **Diffuse**



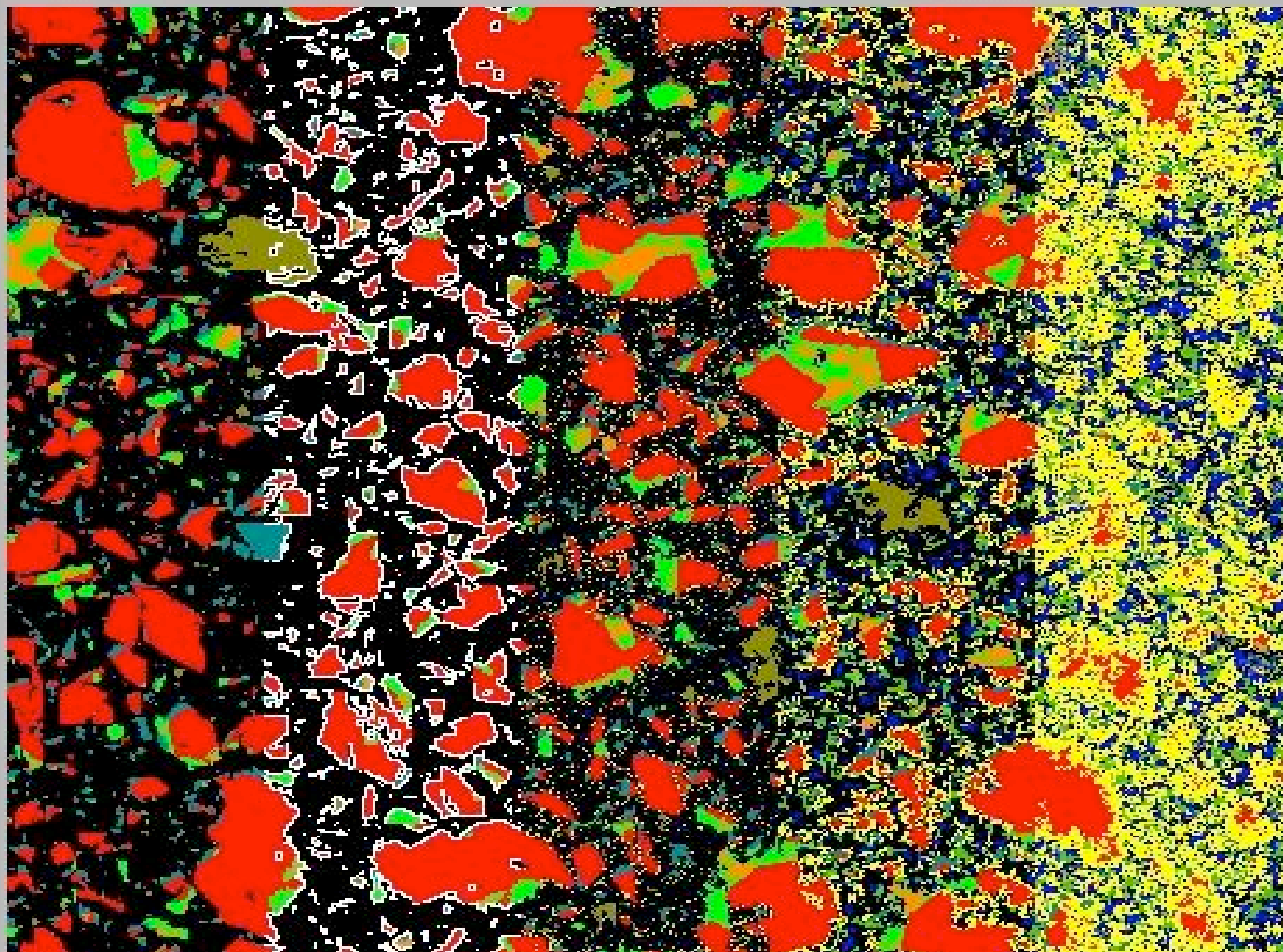
Stepwise random walk on lattice

- **React**



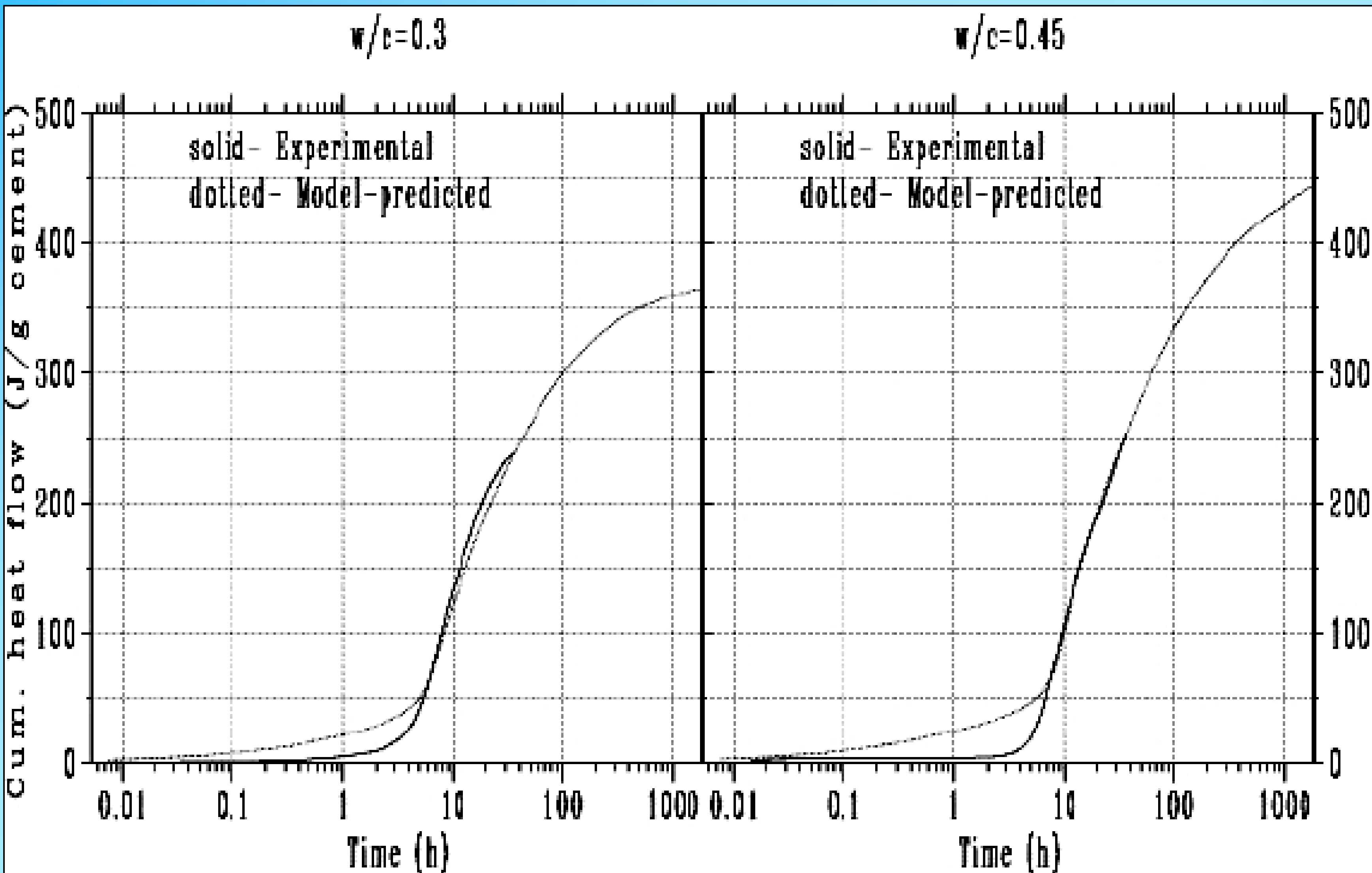
Collisions between agents, governed by reaction “rules”

Illustration of Model Cement Hydration

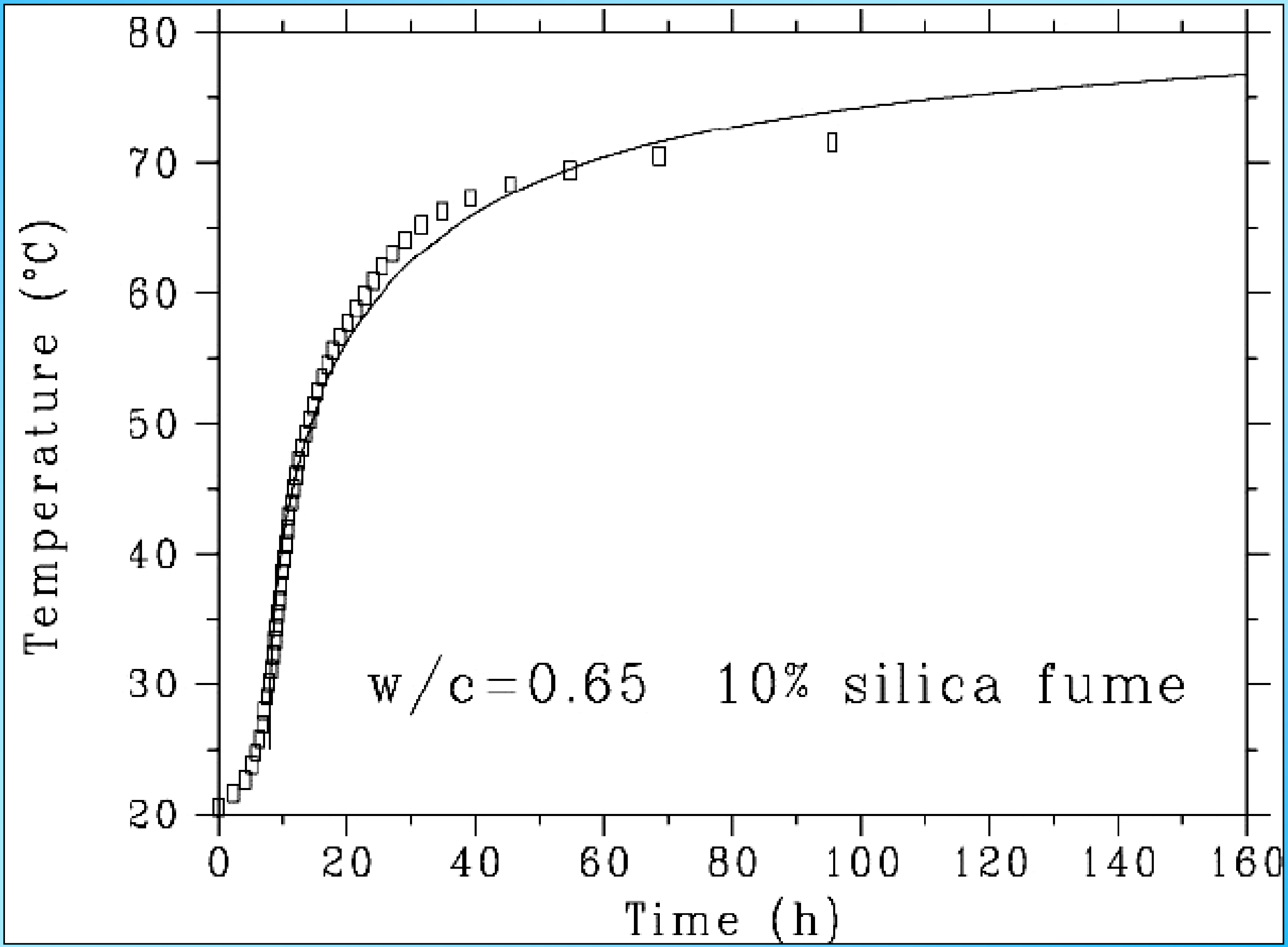


initial/dissolution/diffusion/early/late

Heat of Hydration



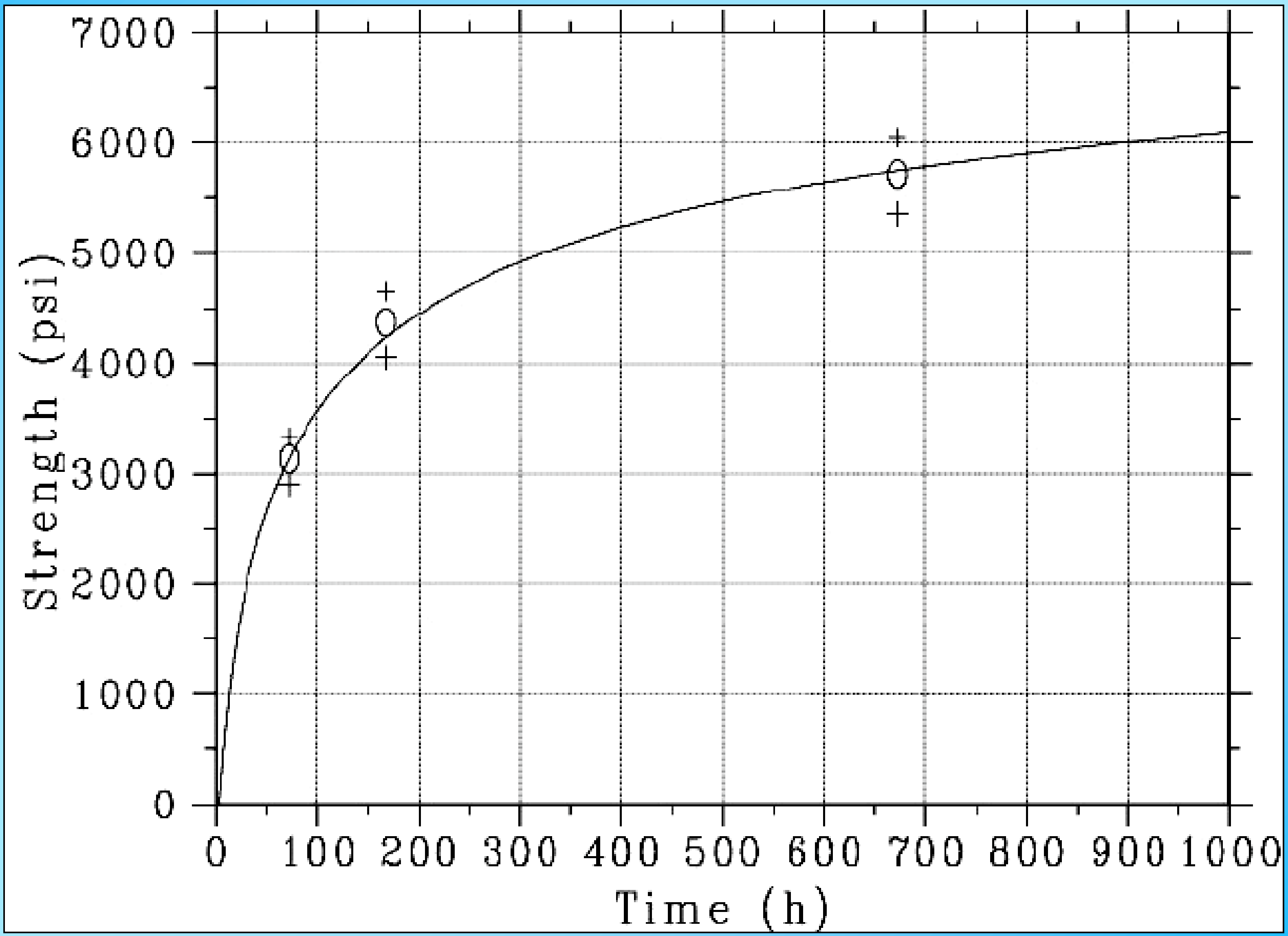
Predicted Adiabatic Heat Signature



Prediction of Compressive Strength

- Use gel-space ratio theory of Powers and Brownyard
  - $X = (0.68 * \_)/(0.32 * \_ + w/c) =$ gel/space
    - directly count gel and space in 3-D microstructure
  - $\__c = A * X^n$ (n=2.6 to 3.0)
- Calibrate A via measured 3-day compressive strength (assume n=2.6)
- Use hydration model to predict X vs. time and calculate 7-day and 28-day compressive strengths to compare to experiment

Prediction vs. Experiment



Example #1

Replacement of coarse cement particles by inert fillers in high-performance concrete

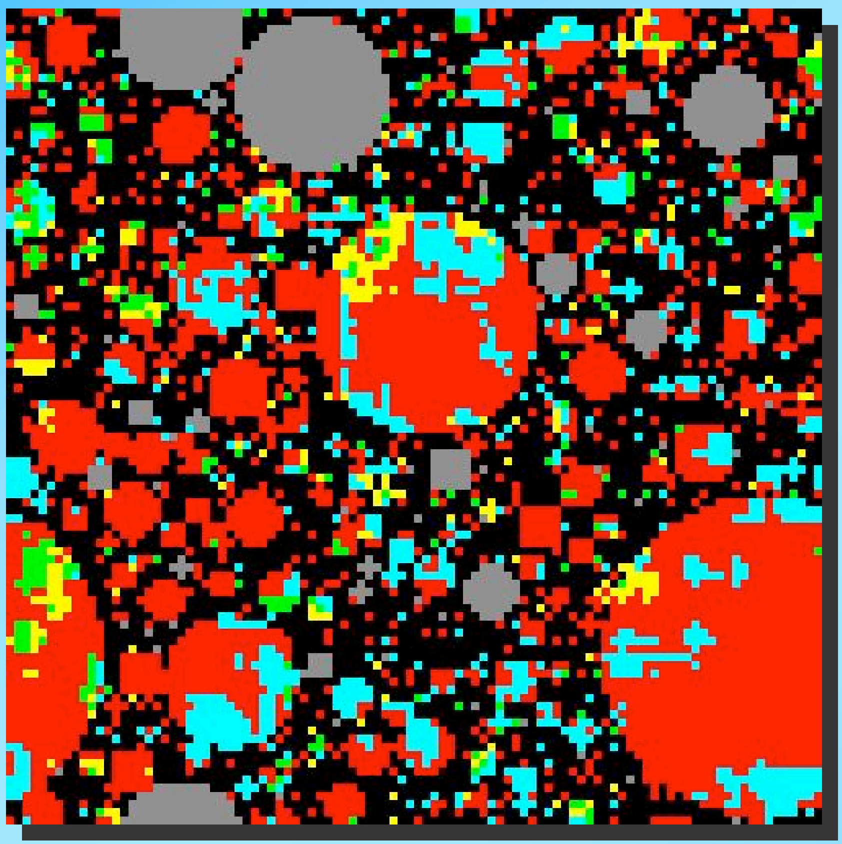
- In low (< 0.38) w/c concretes, there is insufficient space for all of the cement to hydrate
- Thus, in HPCs we are often using expensive cement as a reinforcing filler
- Can we replace a portion of the (coarse) cement by an inert filler without a significant loss in strength in these HPCs?
- Reference: Bentz, D.P., and Conway, J.T., Cement and Concrete Research, Vol. **31**, 503-506, 2001.

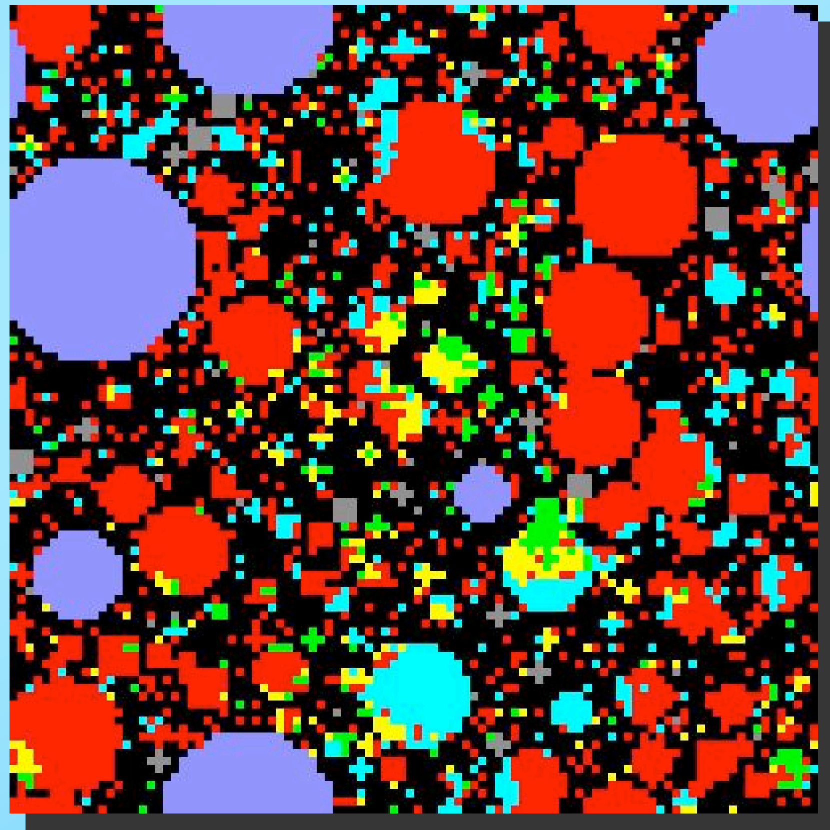
Main Details

- CCRL Cement 135 (68 % C_3S, 17 % C_2S, 7 % C_3A and 8 % C_4AF - 394 m^2/kg Blaine)
- w/s of 0.25 and 0.30
  - 0.30: replace coarsest 14.5 % and 22.3 % of particles (mass basis; particles larger than 20 _m to 27 _m in diameter)
  - 0.25: replace coarsest 20.5 % and 30.8 %
- hydrate for about 200 d of real time using VCCTL
- compare degrees of hydration and predicted compressive strengths (assume unhydrated cement and inert filler contribute equally to strength)

Initial Microstructures: w/s=0.25

No filler | **30.8 % filler**

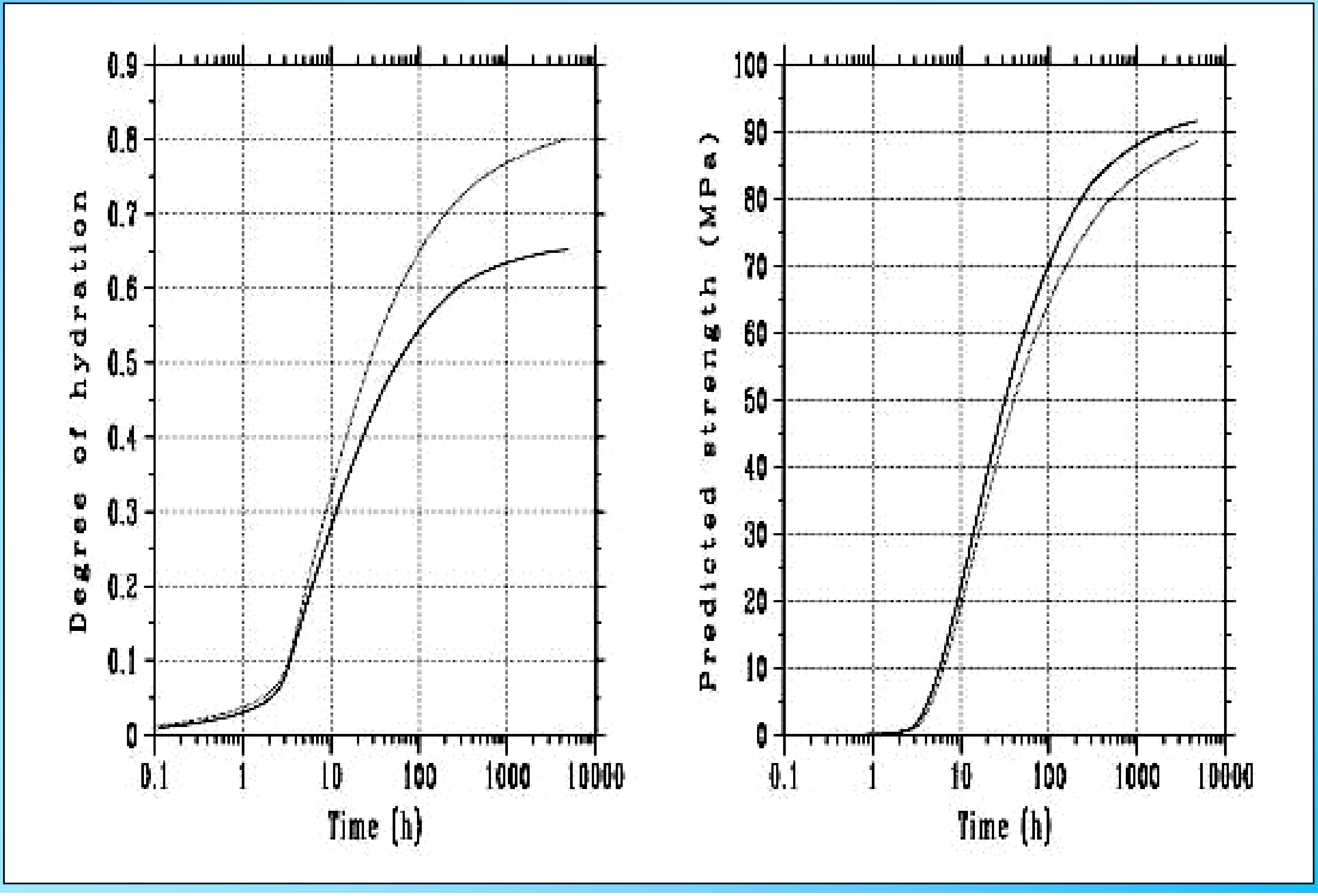




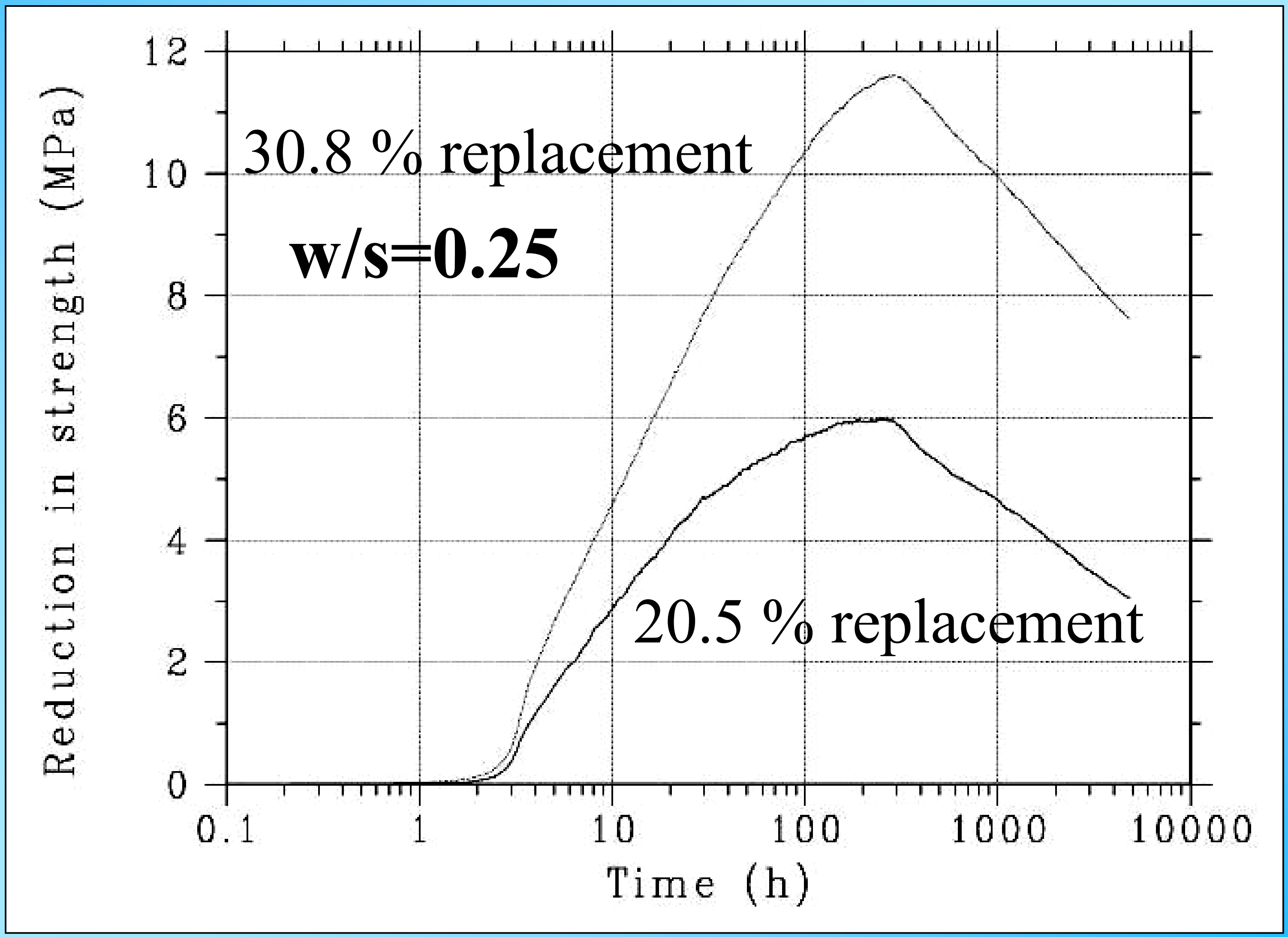
C_3S C_2S C_4AF C_3A Gypsum Inert

Predicted Degree of Hydration and Strength Development

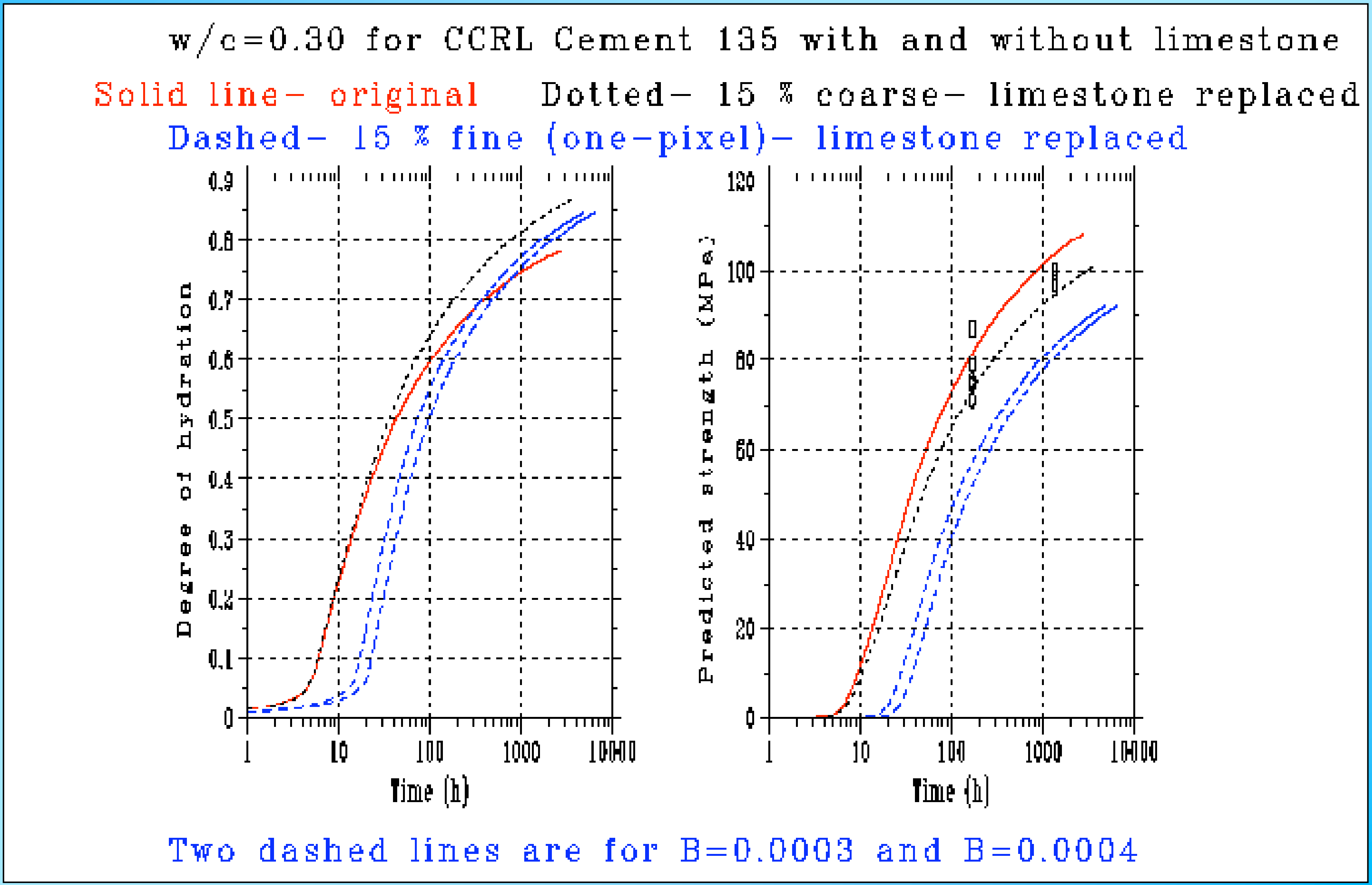
(w/s=0.25 20.5 % replacement: dashed line)



Difference in Compressive Strength



How important is “coarse” particle replacement?



Are these predictions supported by experiment?

- Obtained limestone from OMYA, Inc. and classified it along with CCRL Cement 135 (at 30 _m)
- Prepared high-performance mortars (w/s=0.30) with and without 15 % coarse cement replacement by limestone
- Observed about a 10 % loss in compressive strength at 7 d, but equivalent strengths at 56 d (99 MPa)

Implications from VCCTL

- Appears that one can replace 15 % -20 % of coarse cement particles by inert fillers in low w/s ratio HPCs with only about a 5 MPa reduction in 28 d strength

- VCCTL useful for
  - exploring "what if" scenarios
  - optimizing material systems

Recent extensions

Better understanding ⇔ Improved models

- Addition of limestone reactions
- Addition of slag reactions (some fly ash reactions, silica fume already in model)
- Modelling of pore solution concentration during hydration (K^+, Na^+, pH, etc.) (relates strongly to ASR behavior)

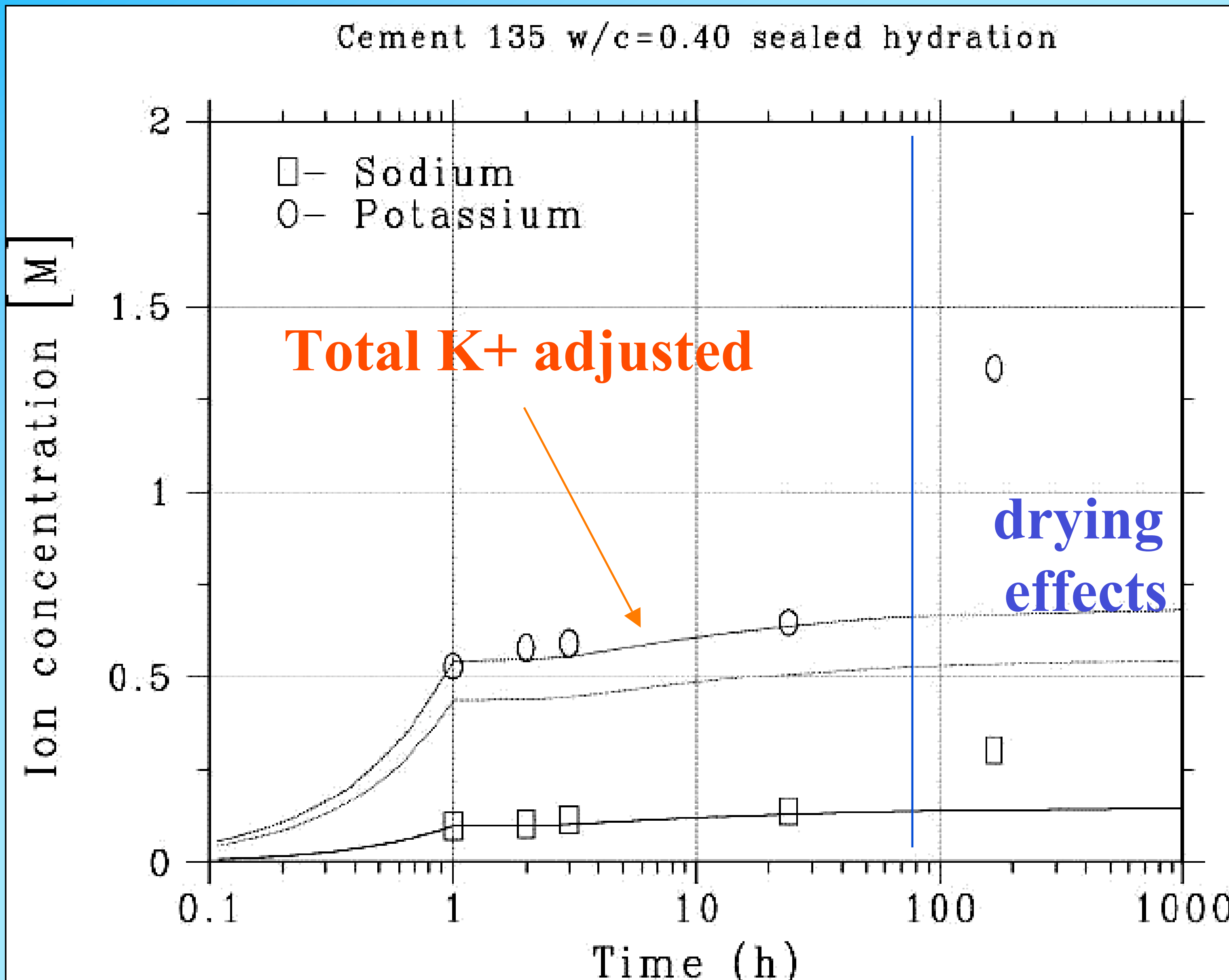
Example: Influence of Alkali Species

- Goal: Link pH (ion concentrations) to hydration kinetics in VCCTL model

- Approach: Add known quantities of alkalis to cement pastes and assess changes in hydration kinetics as measured by non-evaporable water content (w_n)
  - at NIST, Cemex, and Dyckerhoff Zement

Coordinated Modeling with Experimental Validation

- NIST experimental effort
  - Pore fluid expression studies for various cements at various degrees of hydration to assess concentrations of potassium and sodium and pH
- NIST modeling effort
  - Partition alkalis into readily soluble and slowly released components (assume release of the latter $\propto \alpha$)
  - Account for decrease in **capillary pore** and increase in **gel water** during hydration
  - Account for incorporation of alkali ions by C-S-H and AFm phases (Taylor, H.F.W., *Cement Chemistry*, Thomas Telford, 1997.)


Cement 135 w/c=0.40 sealed hydration
□– Sodium
O– Potassium
Total K+ adjusted
drying effects
Ion concentration [M]
0
0.5
1
1.5
2
0.1
1
10
100
1000
Time (h)

Modeling Efforts

- Approach: make the probabilities for dissolution depend on pore solution concentration. For each phase *i*

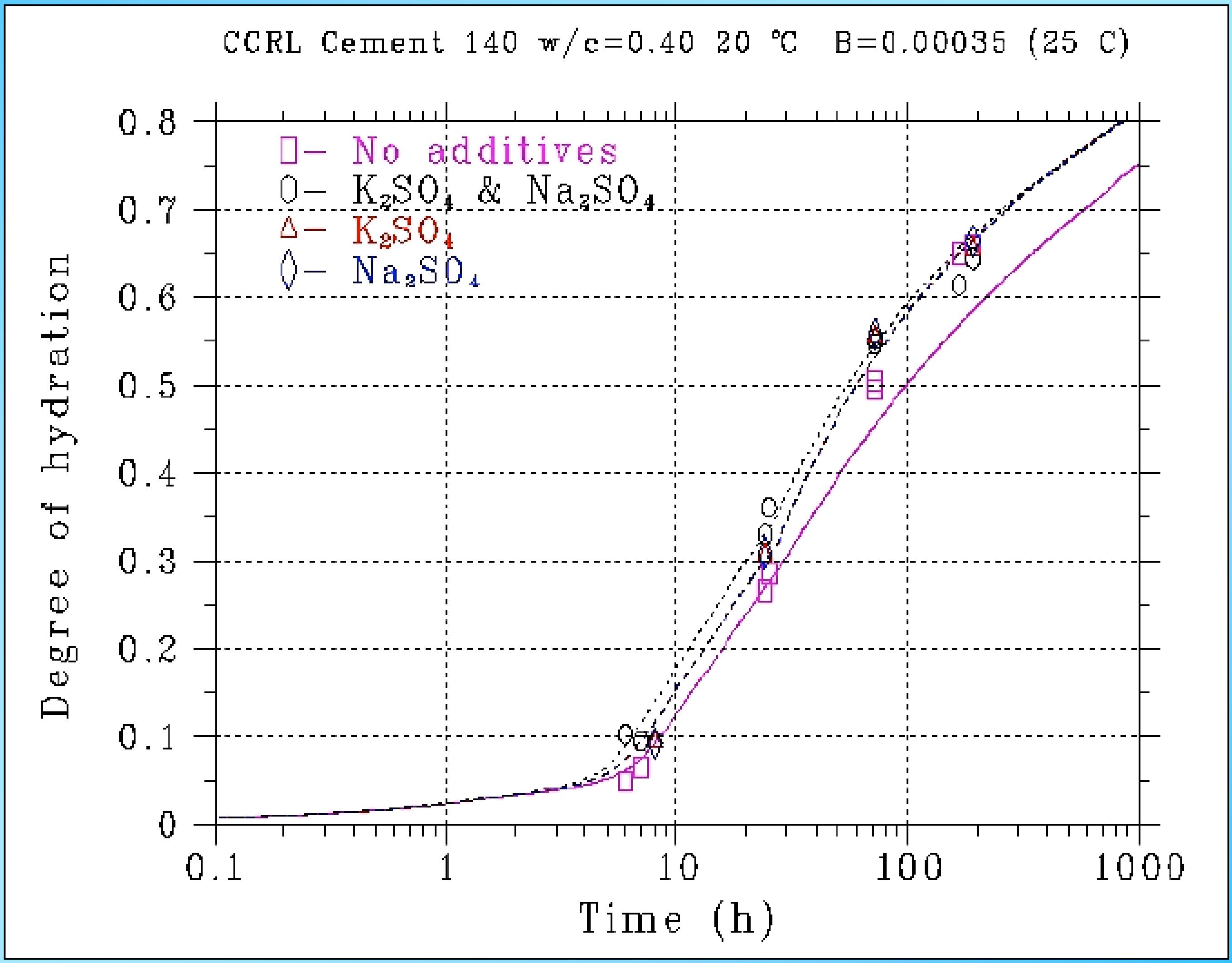
$$P'_i = \frac{P_i(pH=13.25)}{1 + n_i X(pH,[SO_4^{2-}])}, \quad n_i = 0 \text{ or } 1$$

What is X?

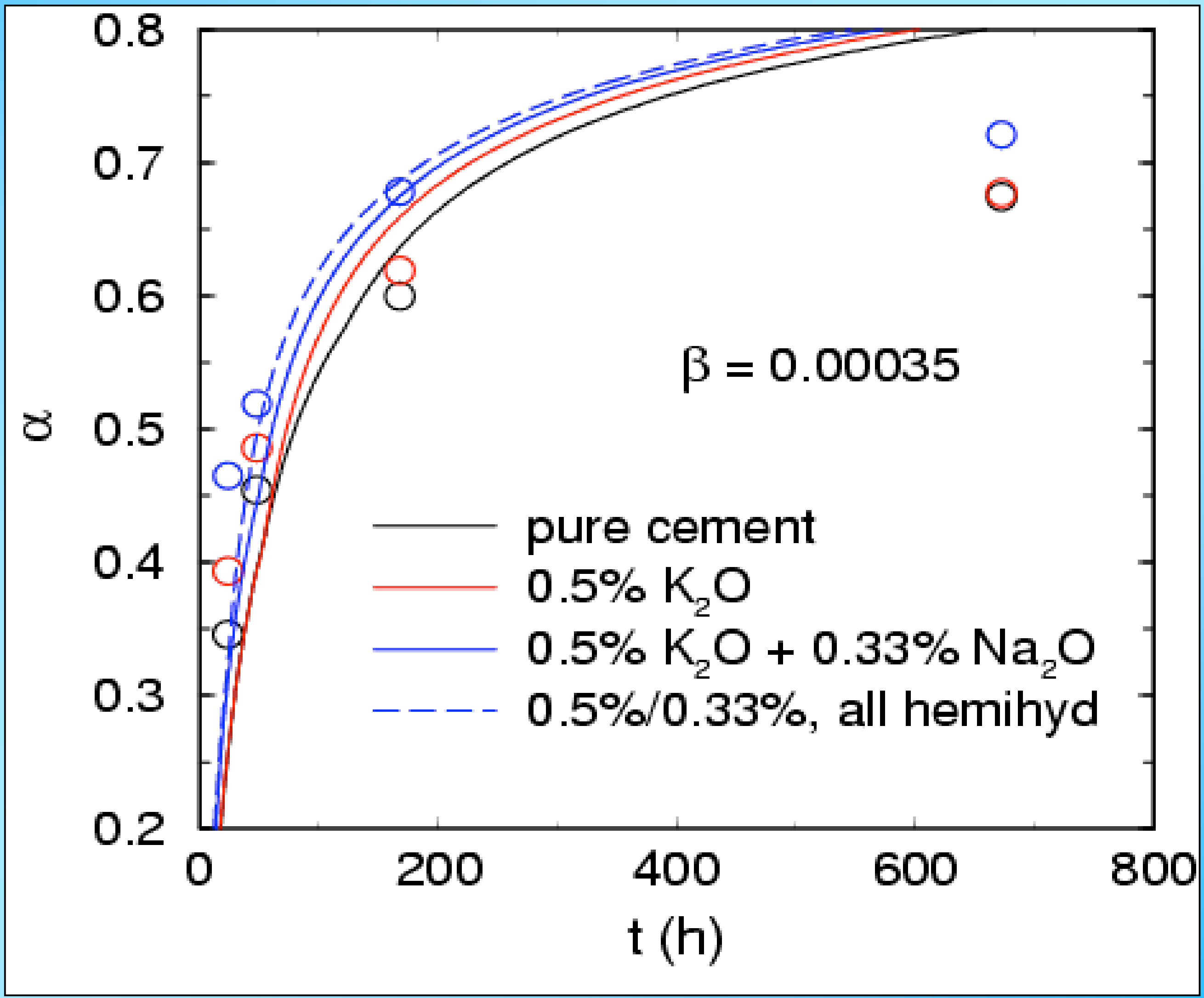
- Function of solution pH and concentration of sulfate ions
- Empirically based, calibrated to data

			pH
X =	$[SO_4^{2-}]$	+ 1.5	$\leq$ 12.5
		+ 1.0	> 12.5
		+ 0.667	> 12.75
		+ 0.333	> 13.0
		+ 0.0	> 13.25
		+ -0.25	> 13.75

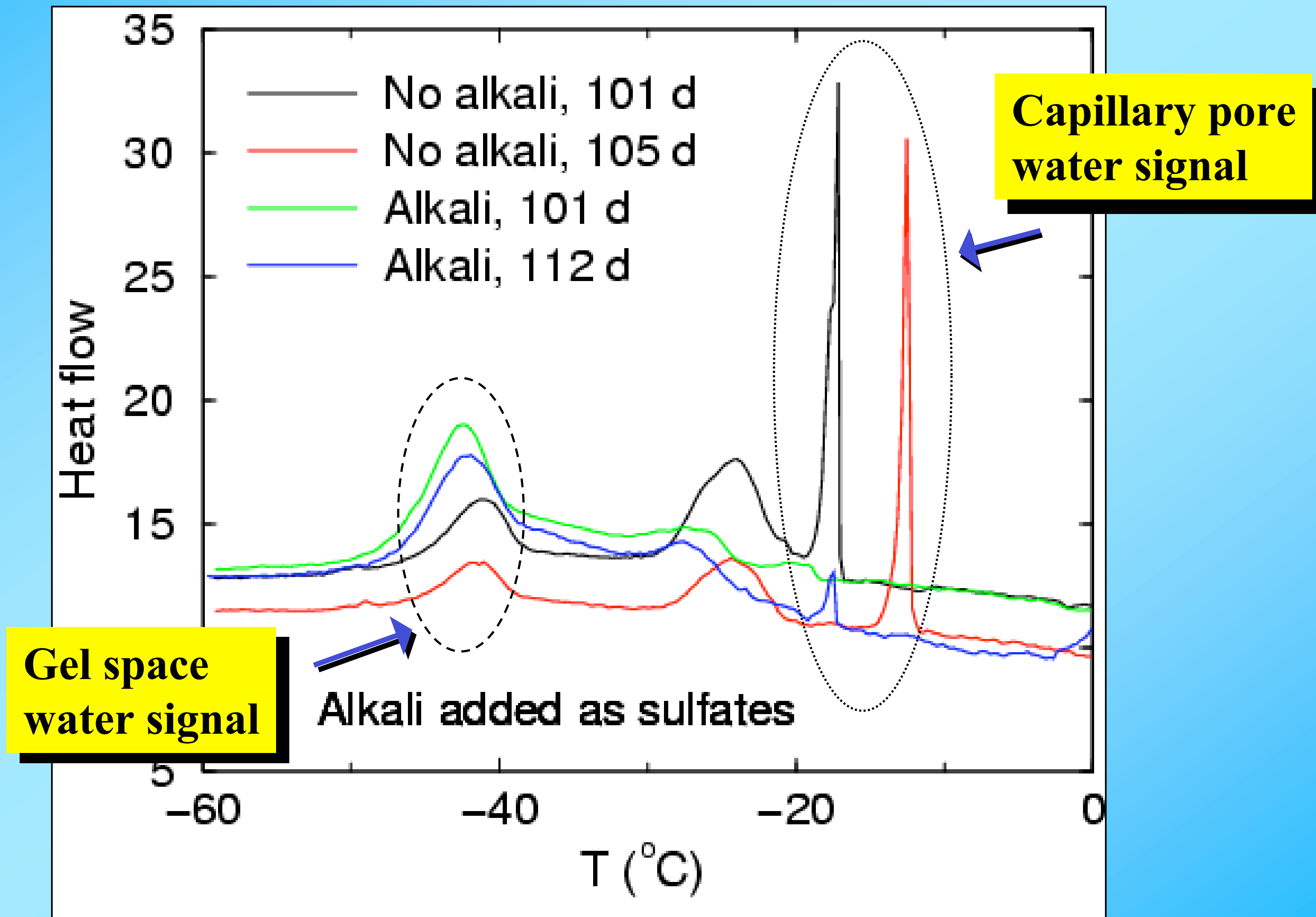
Experimental and Model Results ...



… But Poor Agreement with a Dyckerhoff Cement



Clues from Low-T Calorimetery?



Alkalis in VCCTL Version 3.0

- pH (and pore solution concentration) influences hydration kinetics
  - user selection to turn on or off

- Pore solution conductivity
  - equations added to pHpred.c module
  - procedure based on recent paper by Snyder et al:
    - Snyder, K.A., Feng, X., Keen, B., and Mason, T.O., "Estimating the Electrical Conductivity of Cement Paste Pore Solutions from K^+ and Na^+ Concentrations," submitted to *Cem. Conc. Res.*, 2002.

Ongoing Validation

- Evaluate experimental results generated at Dyckerhoff Zement and Cemex.
- Quantitative XRD analysis of C_3A and C_3S hydration
- Study systems with pozzolans (slag, fly ash, silica fume)
  - good data available from VDZ on absorption of alkalis in blended cement systems
  - pozzolanic C-S-H known to absorb more alkalis than primary (conventional) C-S-H

Module for Rheological Properties of Fresh Concrete

What Do We Wish To Accomplish?

- Ultimately
  - Prediction of concrete rheological properties based on fundamental material variables:
    - cement PSD, w/c, admixtures, paste flocculation, aggregate PSD, etc
  - But this is a very difficult problem, so …

- Currently in VCCTL
  - Prediction of fresh concrete viscosity relative to that of the mortar

Virtual Concrete Rheology

Concrete composition
- Aggregates gradation and shape
- Mineral and chemical admixtures
- Cement type

Rheology
- **Mortar measurements**
- **Computer simulation**

Prediction

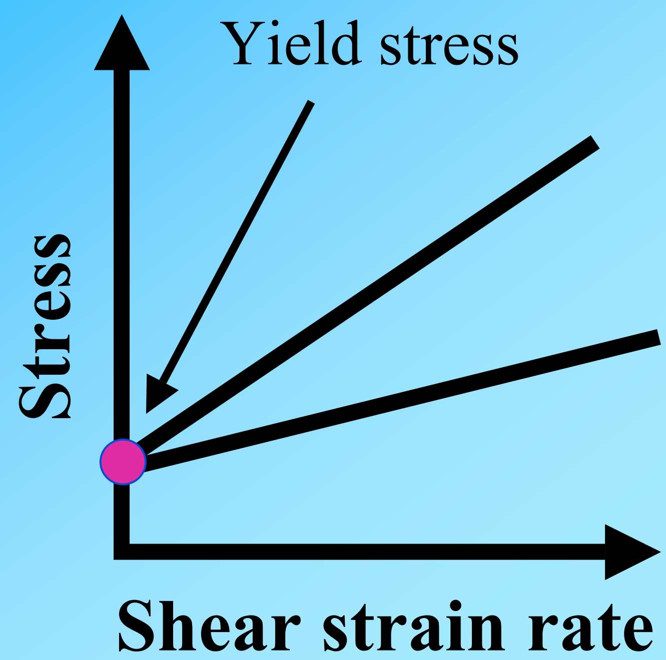
Fresh concrete
- Workability
- Placement
- Finishability

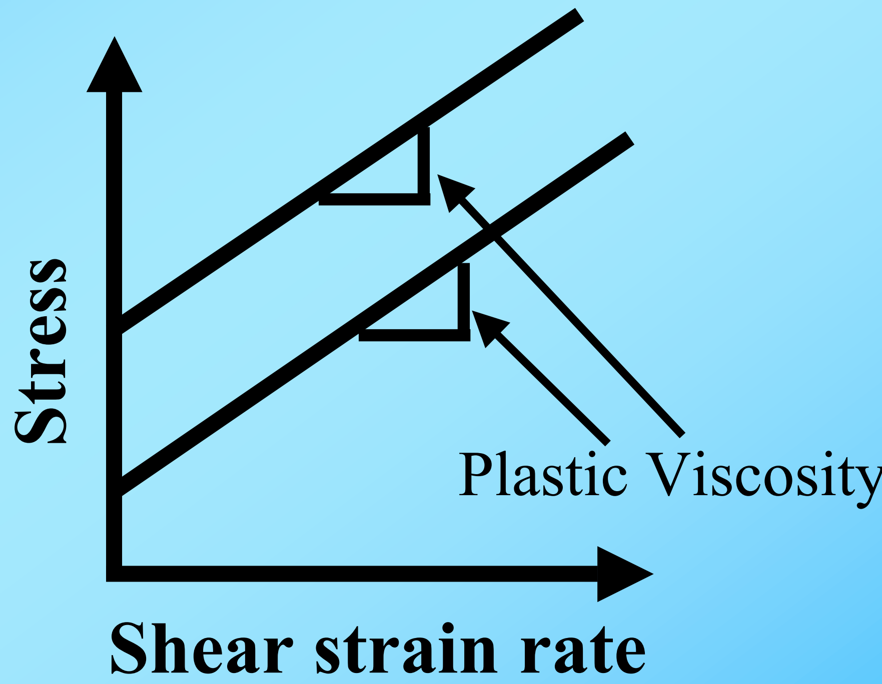
Project Objective

Prediction of fresh concrete rheology

- **Multi-scale approach**
  - Micro: cement in water (Cement Paste)
  - Milli: sand in cement paste (Mortar)
  - Macro: coarse aggregates in mortar (Concrete)

Bingham model concept





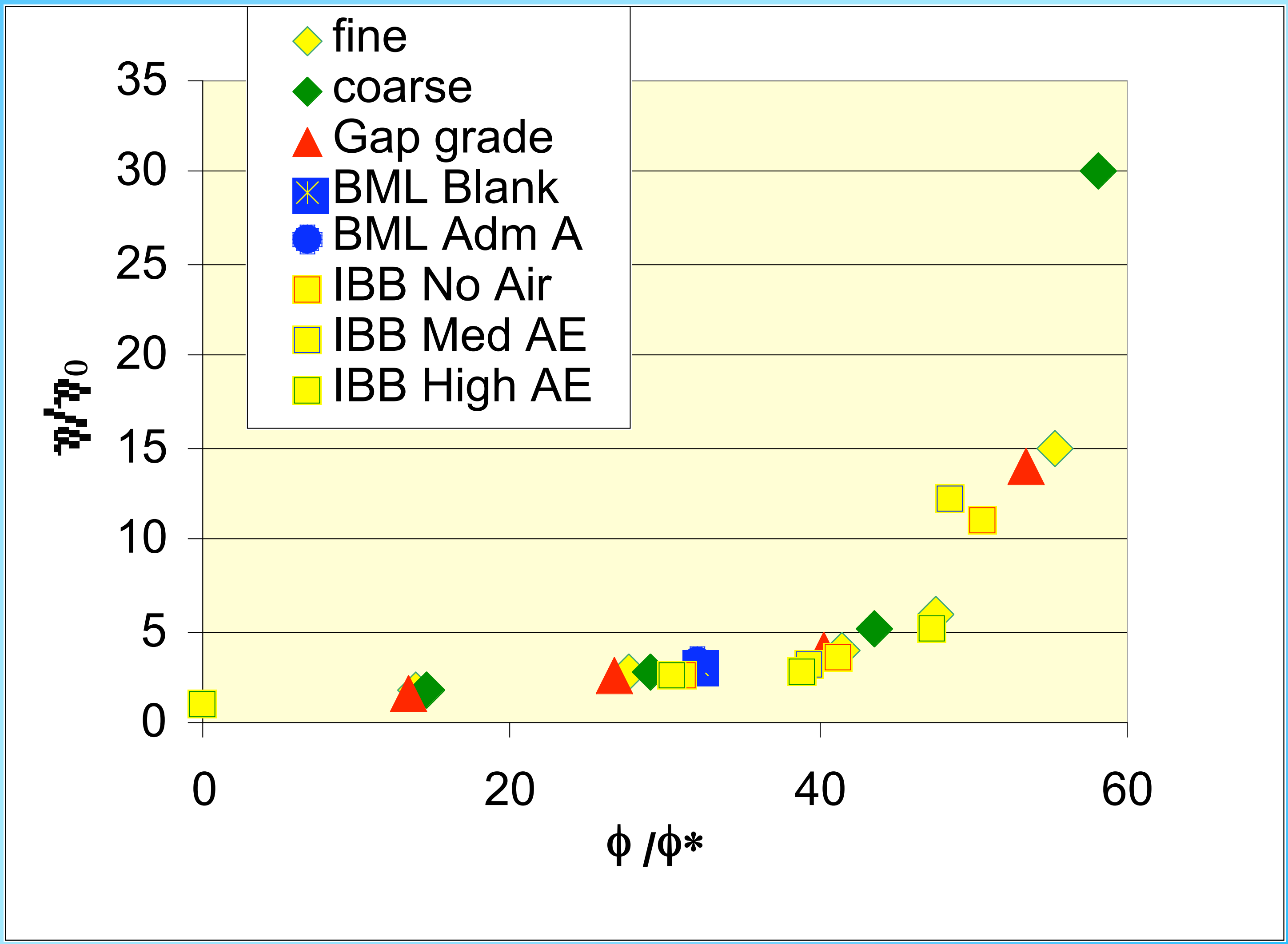
Same yield stress
BUT
different plastic viscosity

Same plastic viscosity
BUT
different yield stress

Relative viscosity

- Relative viscosity = plastic viscosity of concrete divided by plastic viscosity of mortar matrix
- Seems to normalize out rheometer-to-rheometer differences, also normalizes for different mortar matrices
- Relative viscosity is then a material parameter, dependent only on volume fraction, shape, and sieve analysis of aggregates

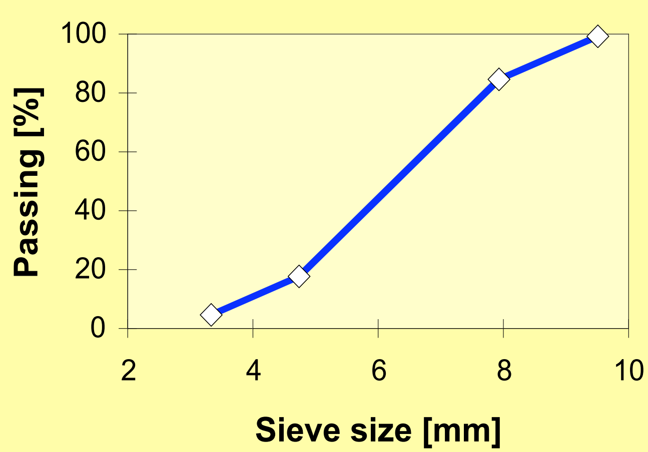
Relative viscosity



From gradation to viscosity: a database

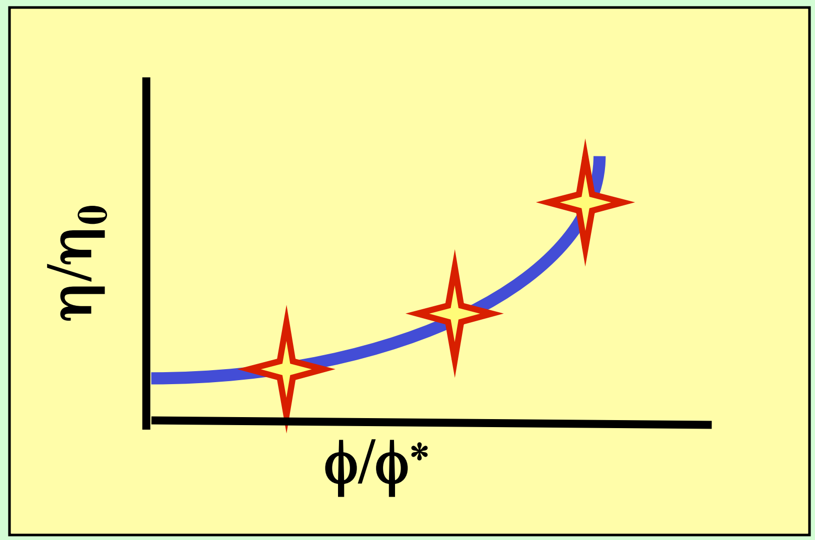
Input: search by

Coarse aggregates size distribution



Output

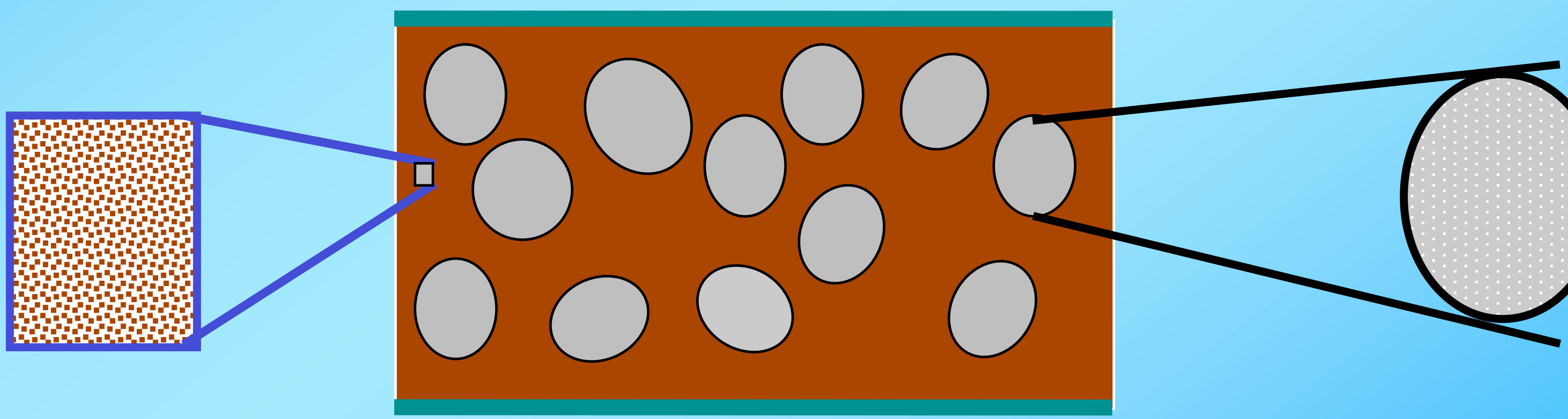
Relative viscosity vs. Solid Fraction



Concrete Rheology Model: Dissipative Particle Dynamics

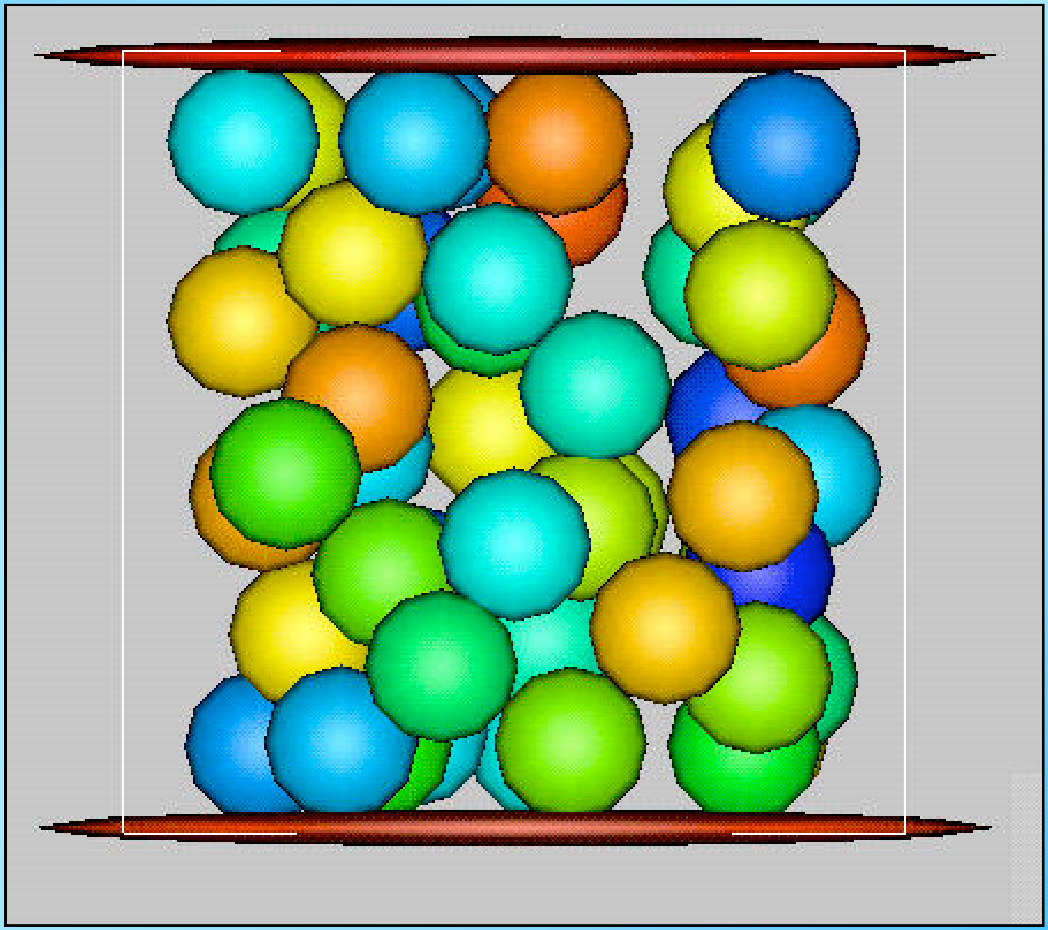
Brownian Dynamics + Momentum Conserving Collision

Hydrodynamic Behavior

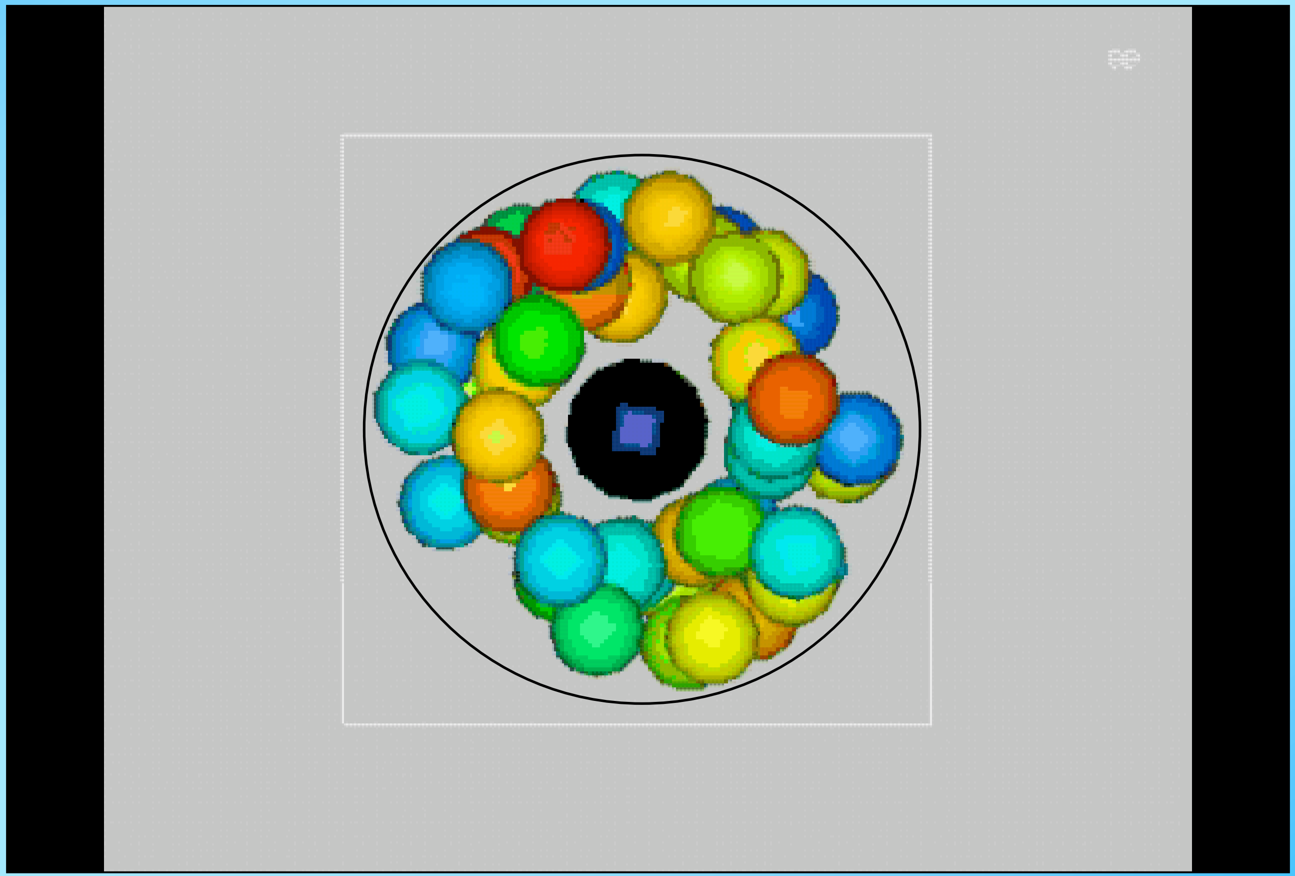


Model developed by N. Martys (NIST) based on an algorithm by Hoogerbrugge and Koelman (1992)

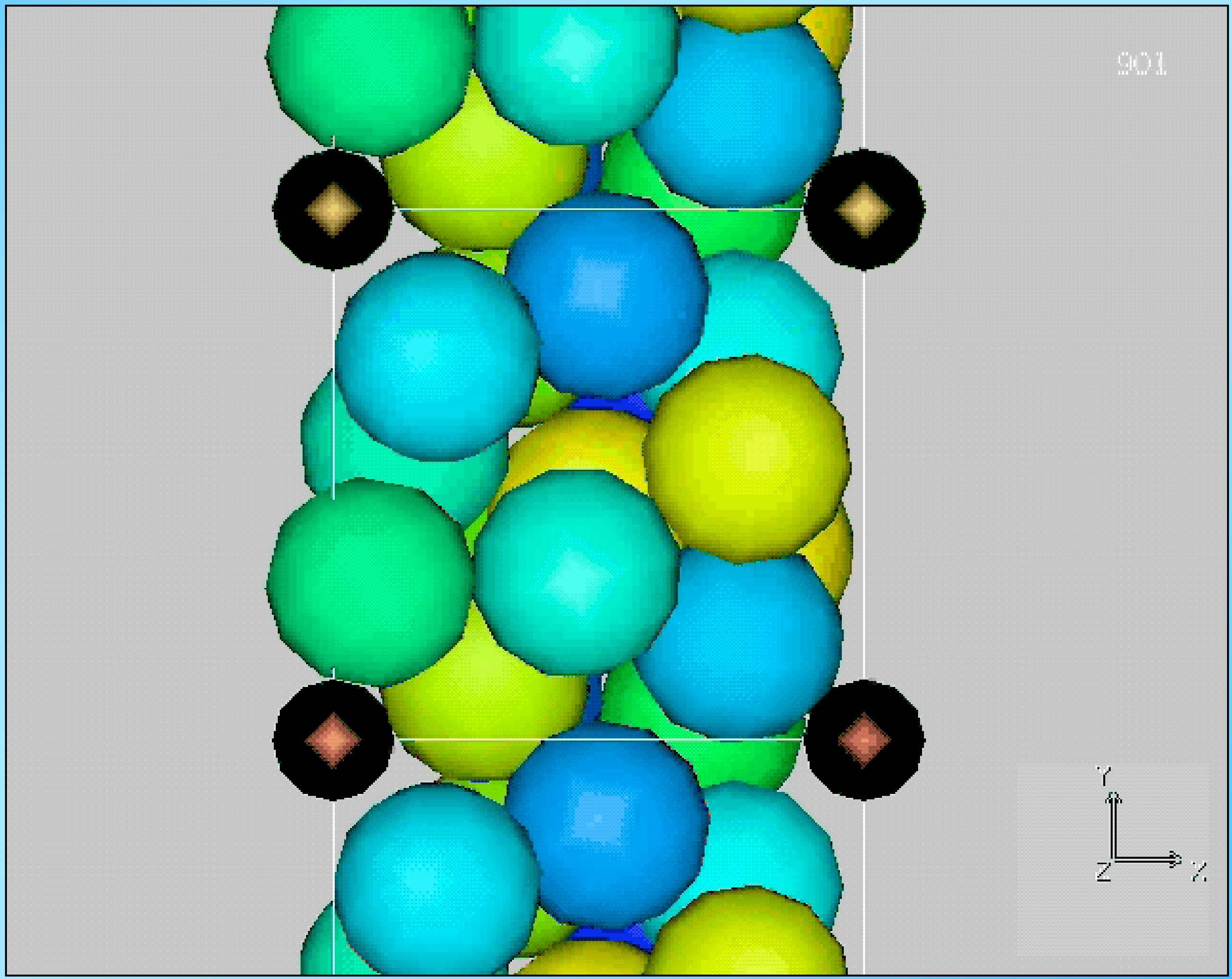
Parallel Plate rheometer



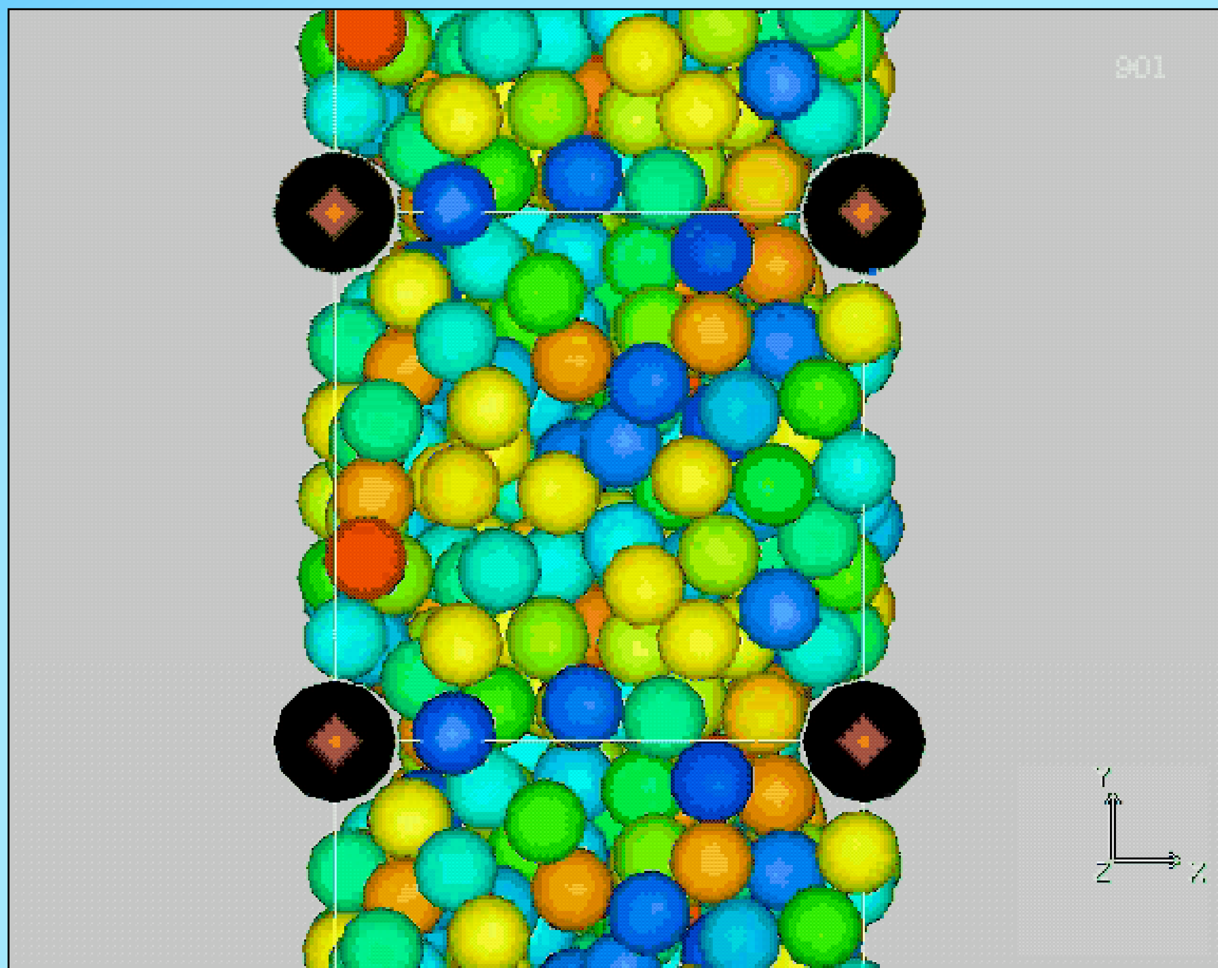
Coaxial Rheometer



Concrete Flow: diam. 0.5



Concrete flow: diam. 0.2

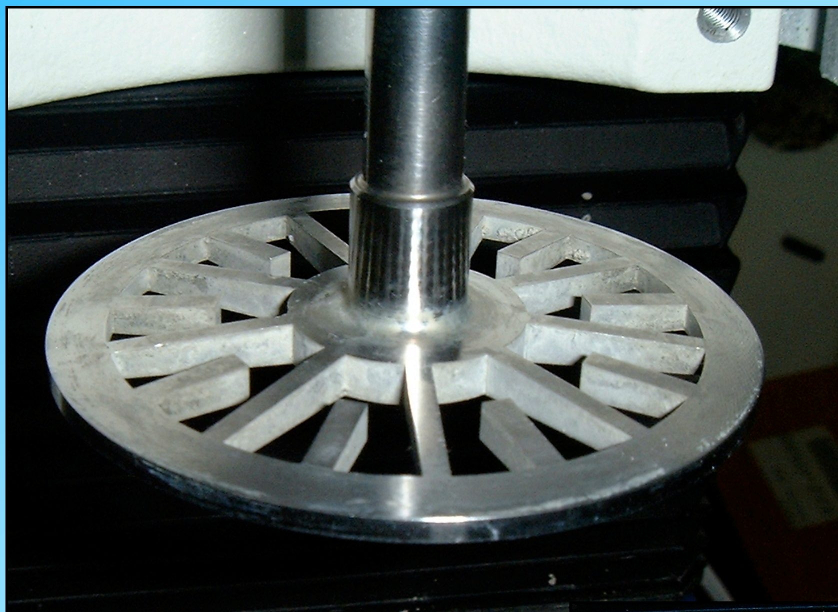


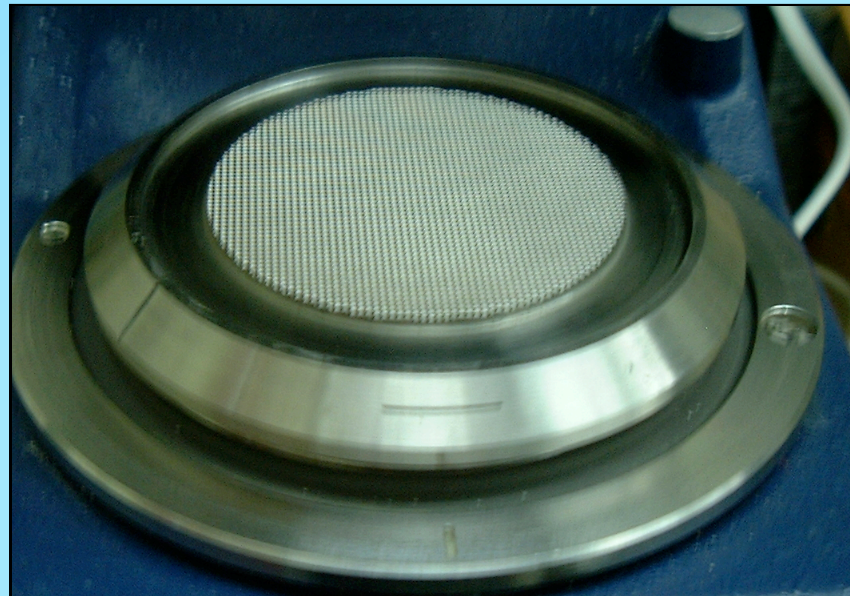
Pretty Simulations, But Are They Any Good?

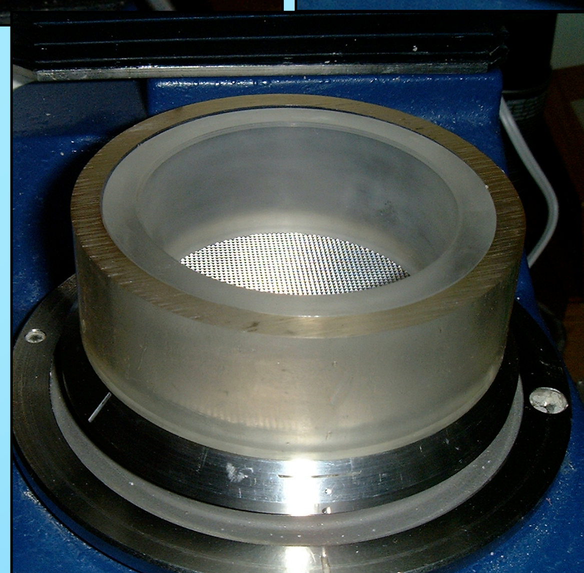
- We require experimental methods to measure the rheological properties (yield stress, viscosity) of fresh mortars and concretes

- Must be reliable and reproducible to provide model validation.

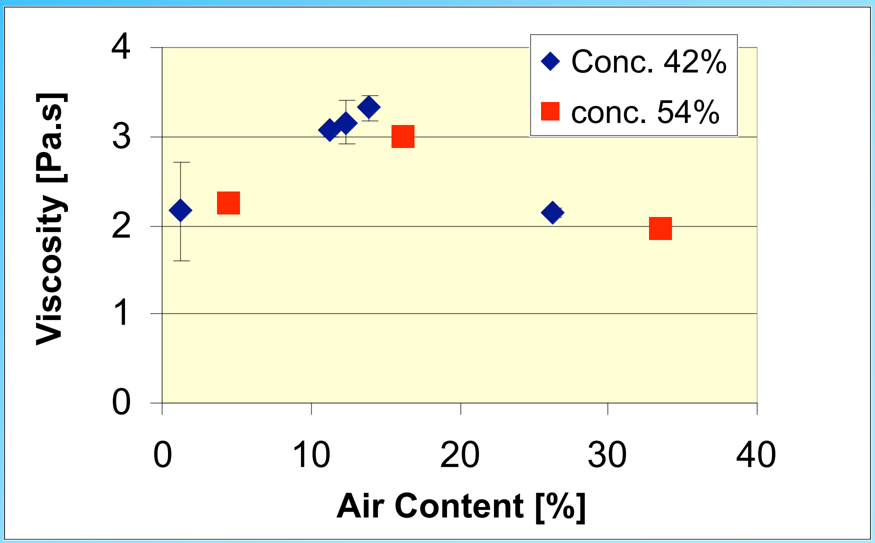
Mortar rheometer



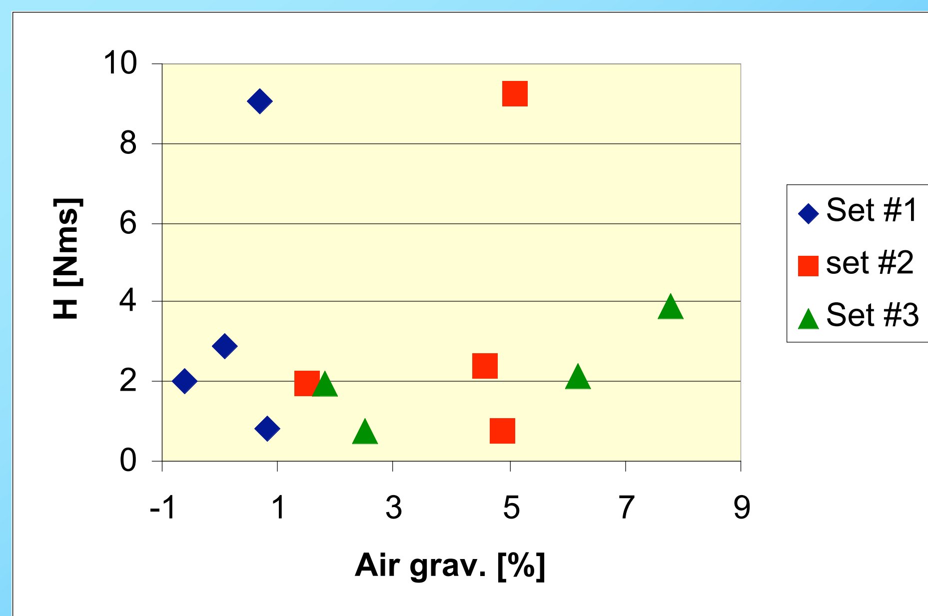




Viscosity as function of air



Mortar



Concrete

Where rheology work is heading

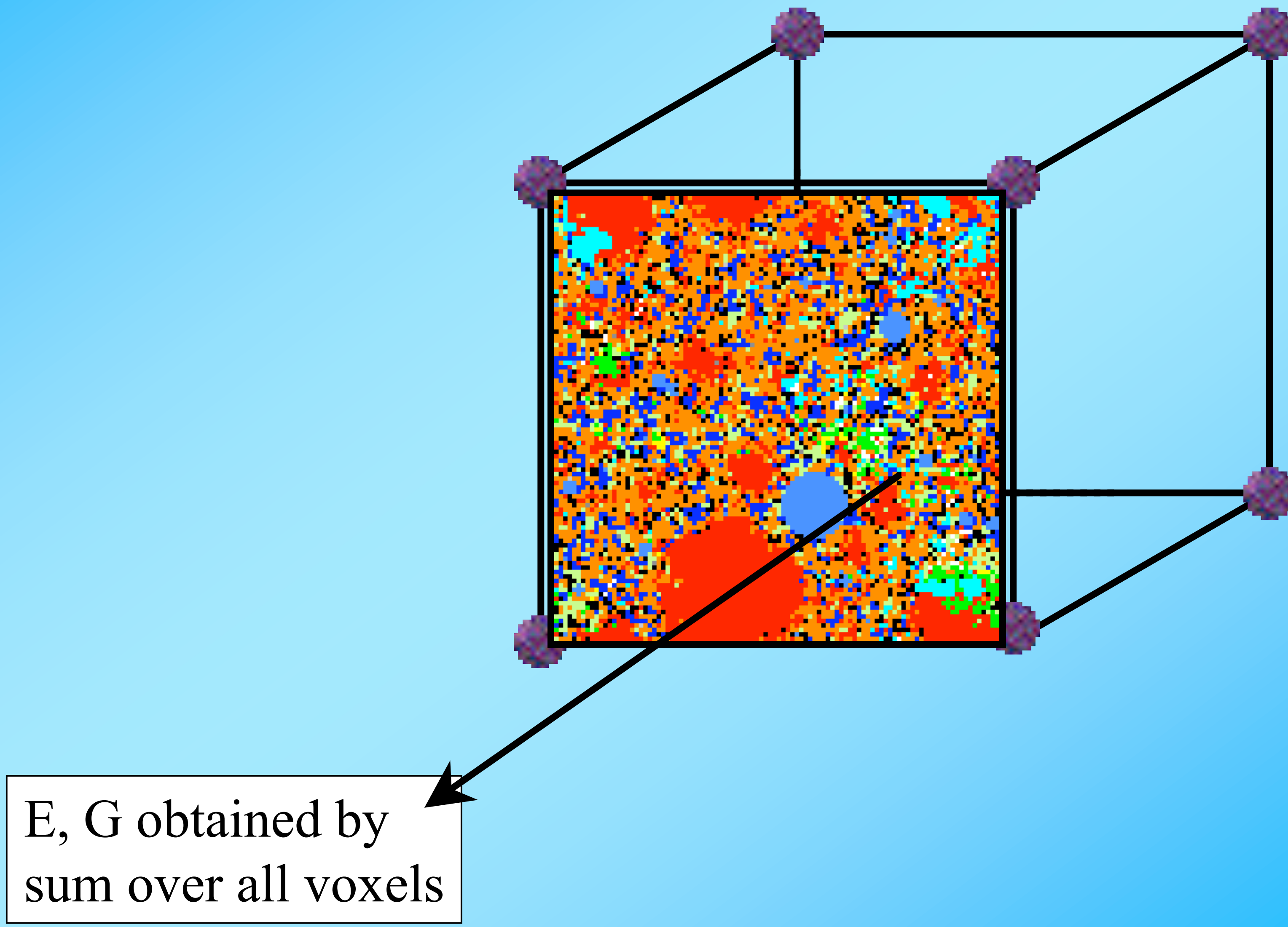
- Method to **measure in mortar** the influence of air, chemical, mineral admixtures
- **Simulation** of various geometries of rheometers or flow between rebars
- **Possible quantitative link** between all rheometers and mortar through the relative viscosity

Elastic Properties of Cement Paste

Elastic properties of cement paste

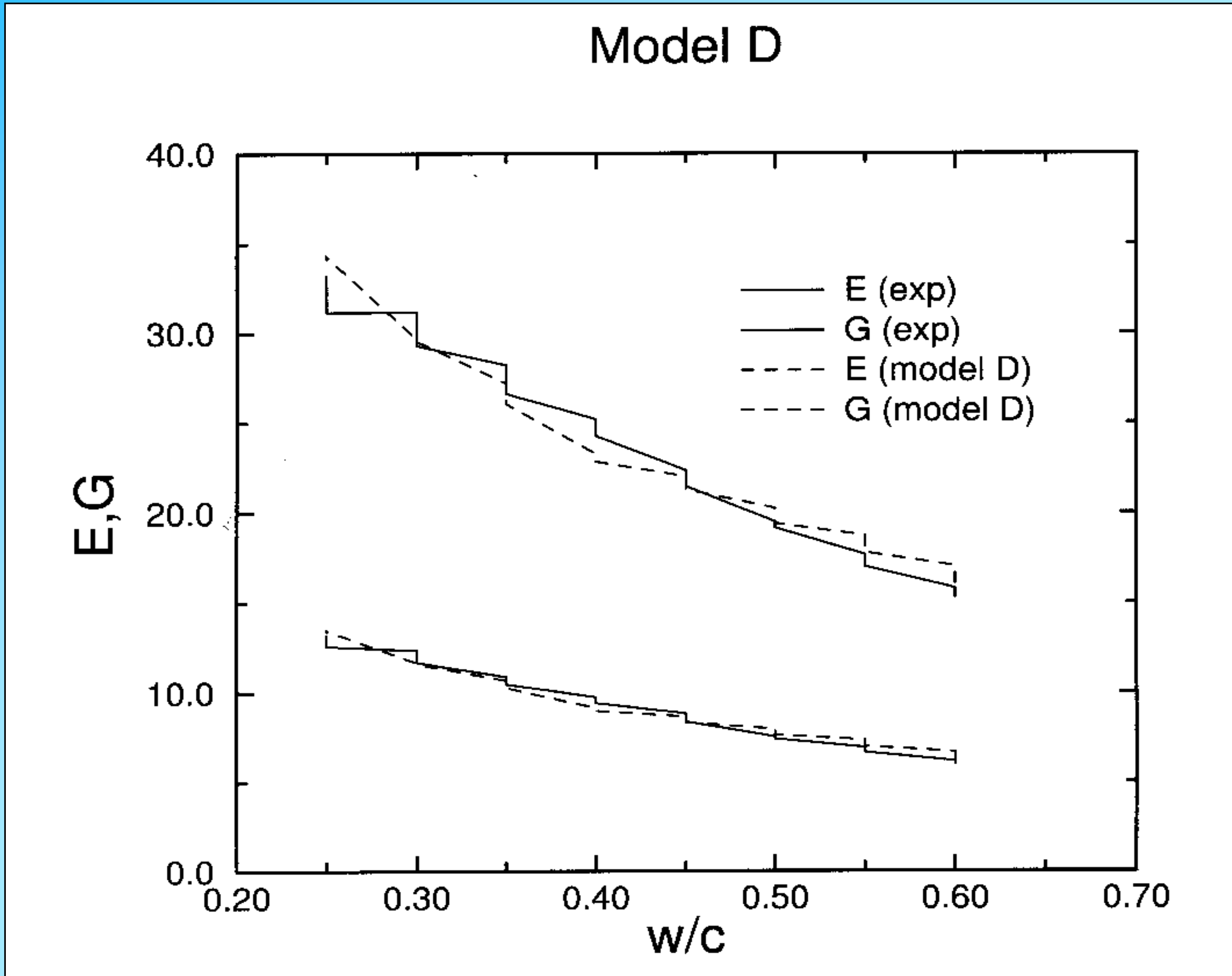
- Combine:
  - measurements of the elastic properties of individual phases and cement paste at various degrees of hydration
  - digital-image-based modelling of cement paste microstructure
  - finite element computation of cement paste elastic moduli
- To result in a predictive tool for cement paste and concrete as part of the VCCTL
- First version is in VCCTL 2.0
- Working with S. Shah of Northwestern (ACBM) to link with compressive strength

Each voxel is a tri-linear finite element



Individual phase moduli

- Some cement minerals in the geology literature, or have been measured (Lafarge) or being worked on
- Good ultrasonic data for CH and ettringite
- Nanoindentation gives $E_{C\text{-}S\text{-}H} \approx 25\text{-}30$ GPa
- Good ultrasonic data for C_3S shows that nanoindentation seems to overestimate E slightly, so take $E_{C\text{-}S\text{-}H} \approx 22$ GPa
- Do C-S-H moduli change with age? Probably yes, but no evidence for how much, so neglect for now



Model D
40.0
30.0
20.0
10.0
0.0
E,G
0.20
0.30
0.40
0.50
0.60
0.70
w/c
E (exp)
G (exp)
E (model D)
G (model D)

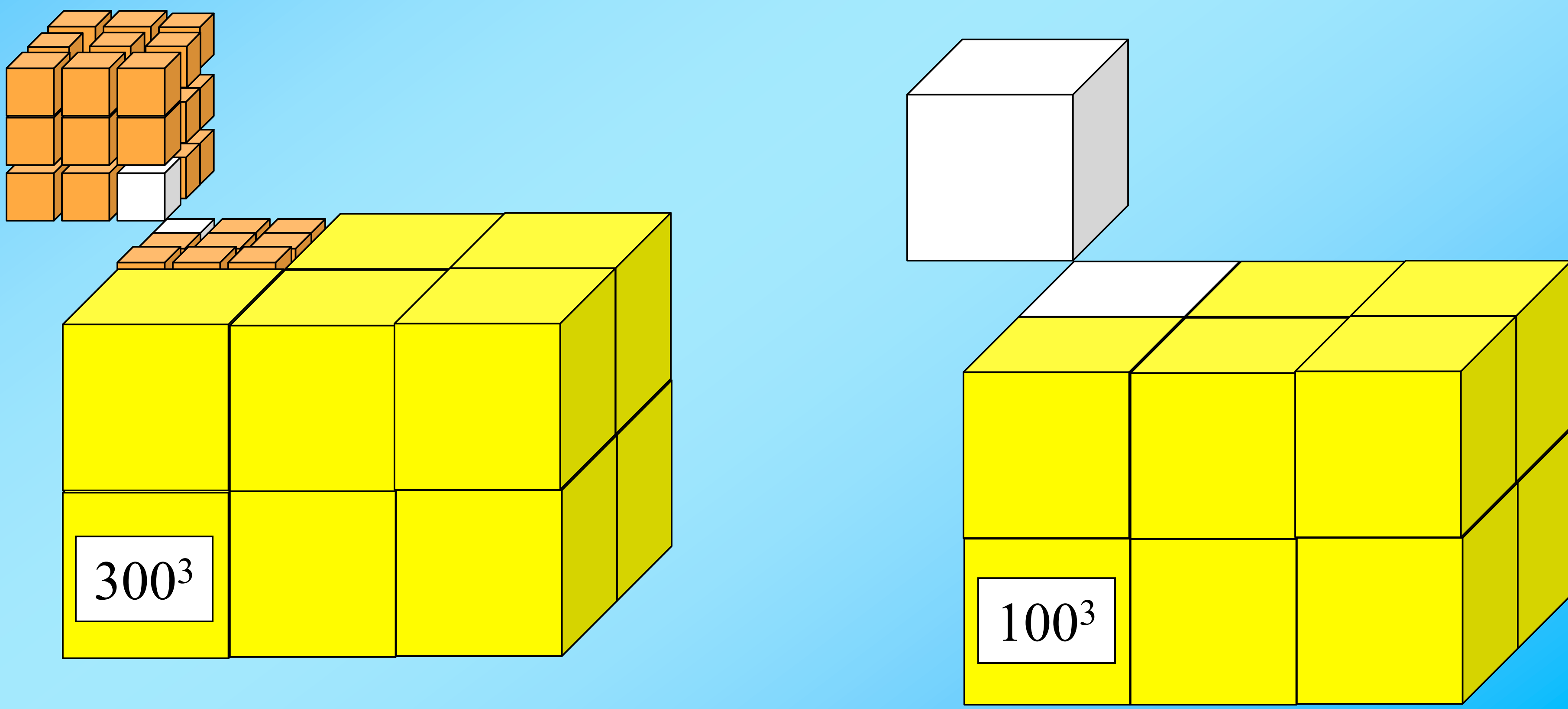
Data comparison (w/c=0.5)

	Experiment		Unmodified model microstructure	
α	E(GPa)	G(GPa)	E(GPa)	G(GPa)
0.0	0.0	0.0	3.6	1.3
0.20	2.1	0.8	8.9	3.4
0.35	6.9	2.7	12.6	4.9
0.50	11.0	4.4	15.3	6.0
0.65	15.4	6.1	17.4	6.8
0.80	18.9	7.5	19.0	7.5

Digital Resolution

- Most early-age problems apparently due to digital resolution.
- Solution - go to higher resolution (i.e., 200^3, 300^3, etc. - we are adding the option of higher resolution to the VCCTL code)
- Scalar code can do systems above 100^3, but longer run-times and memory-intensive requirements restrict size of feasible systems
- Solution: Parallel code, using MPI protocols and extensive re-design of FORTRAN
- Runs on distributed memory (Linux) computers, excellent speed-up and accuracy
- Allows higher resolution cement paste systems to be studied elastically

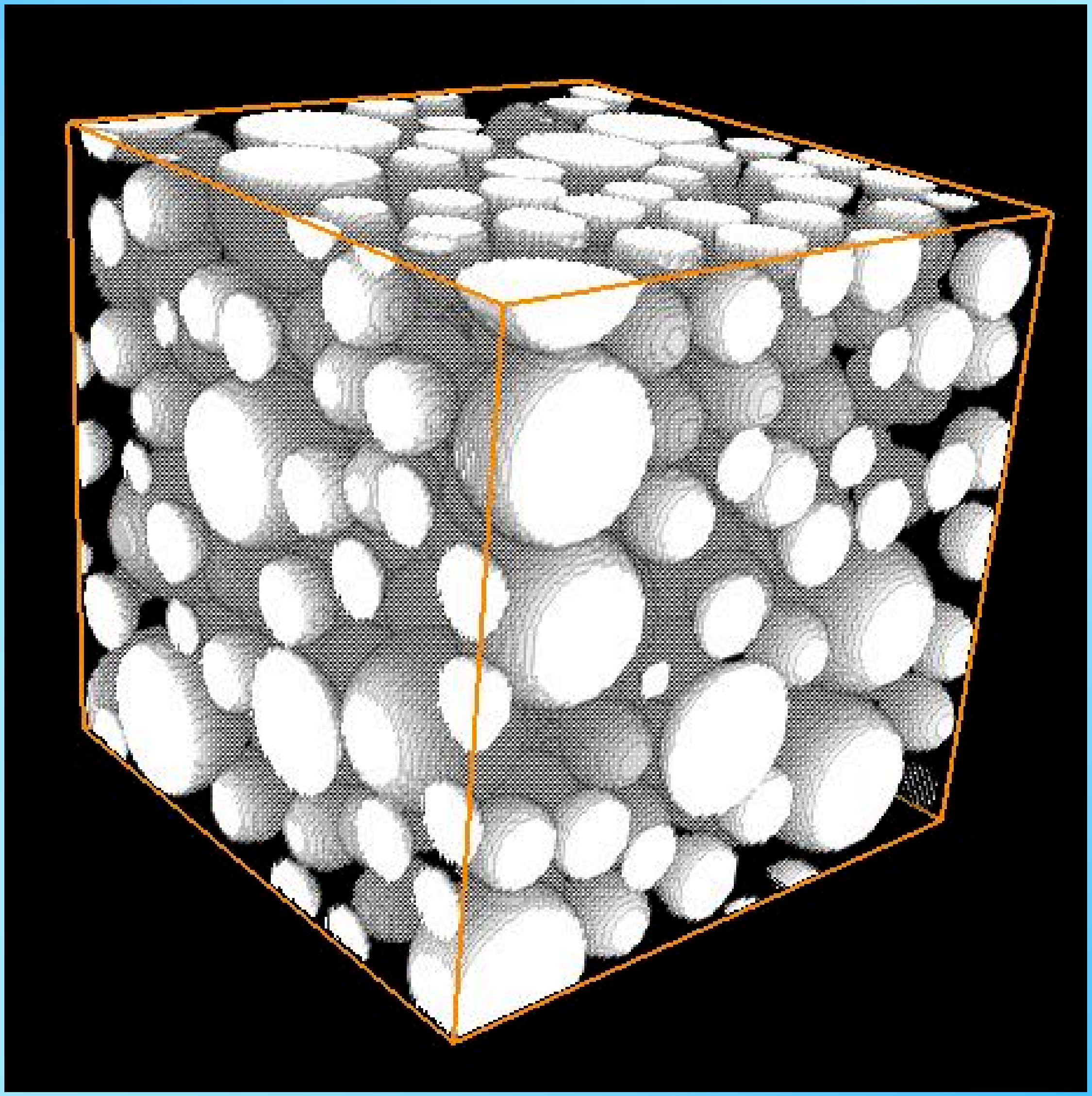
Higher resolution allows artificial connections to be easily “broken” without disturbing microstructure as much as in 100^3 case



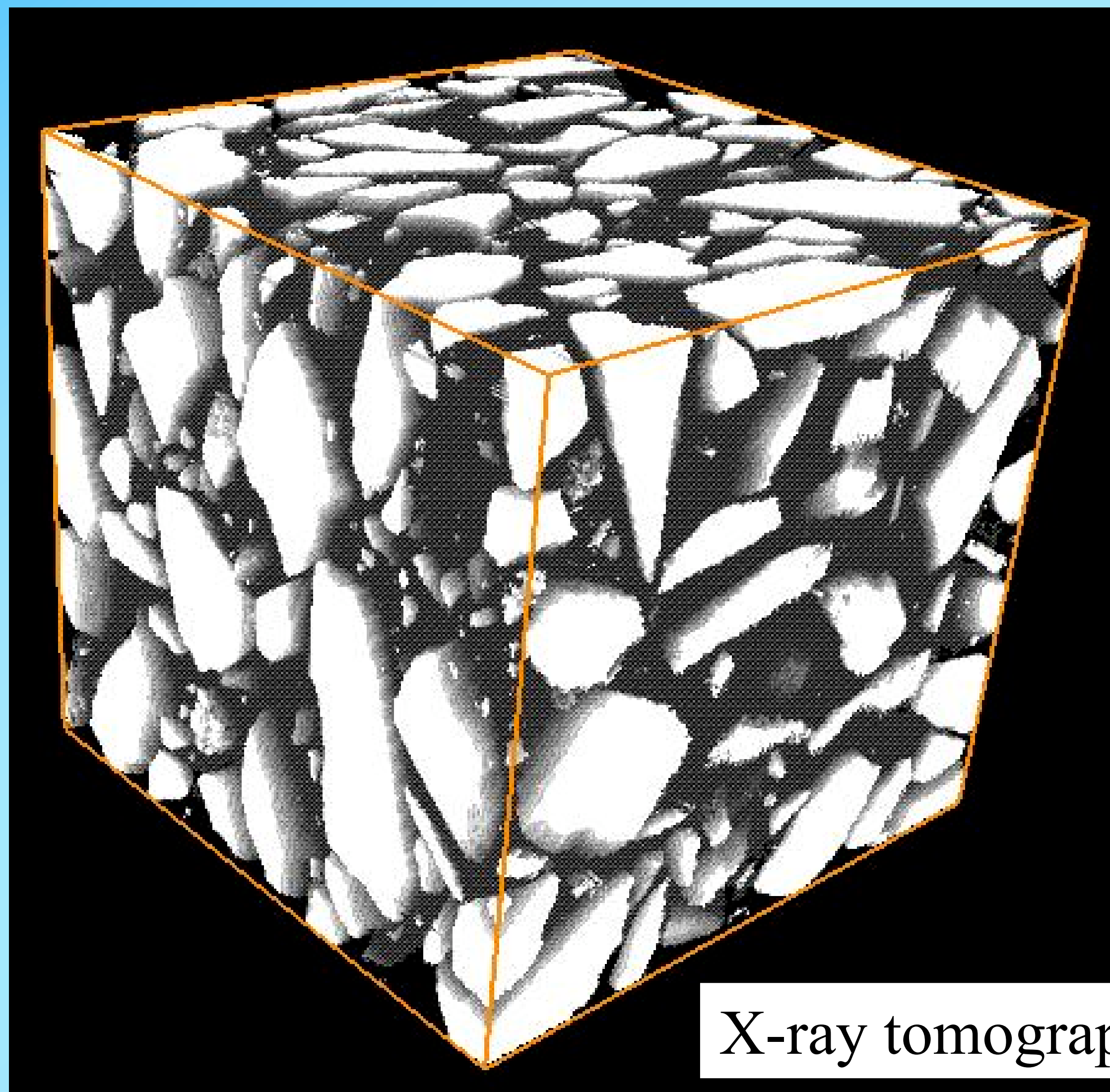
Aggregate shape analysis

(in collaboration with International Center for Aggregates Research)

Model aggregate shapes



Realistic aggregate shapes



X-ray tomography (FHWA)

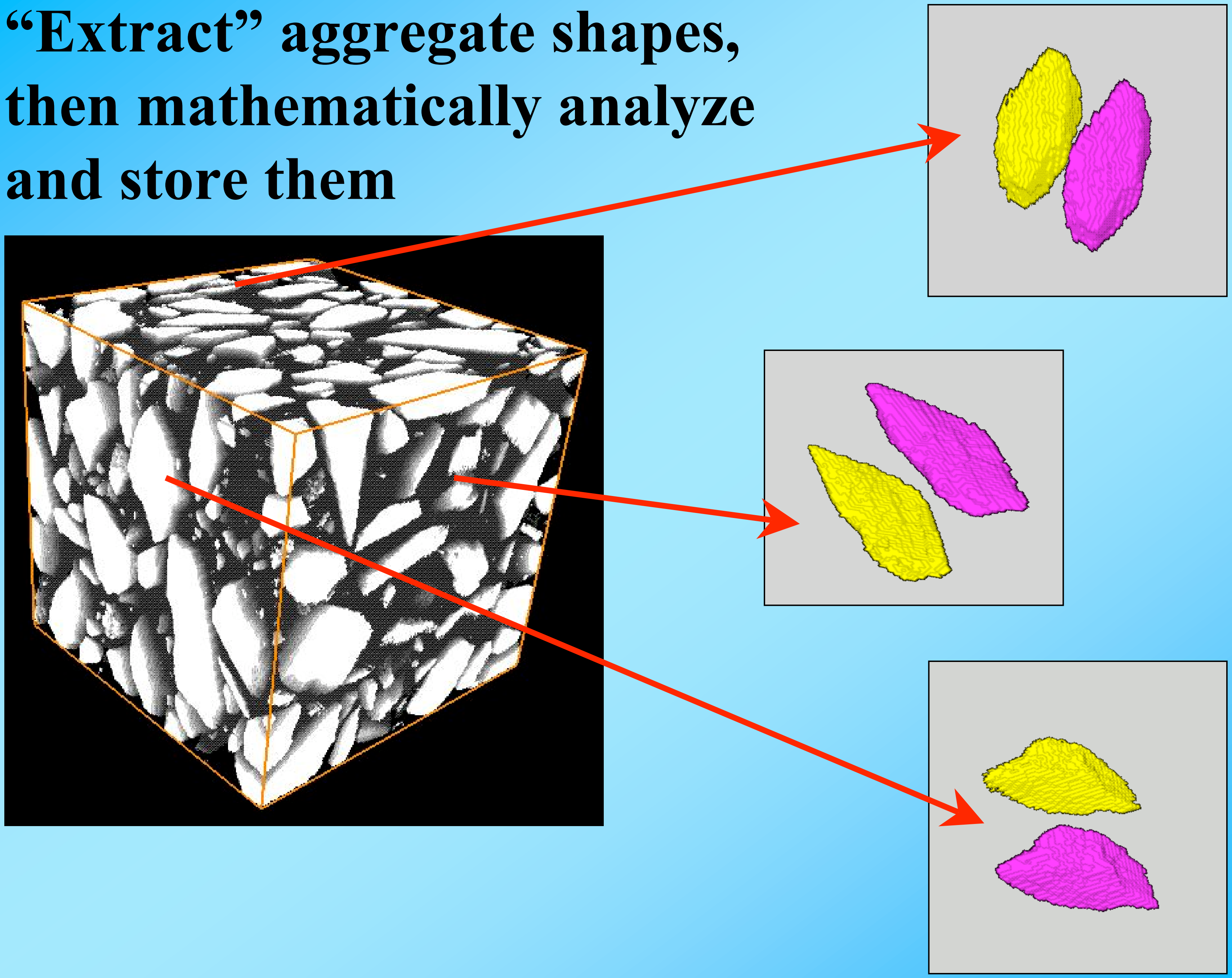
Aggregate shape: Does it matter?

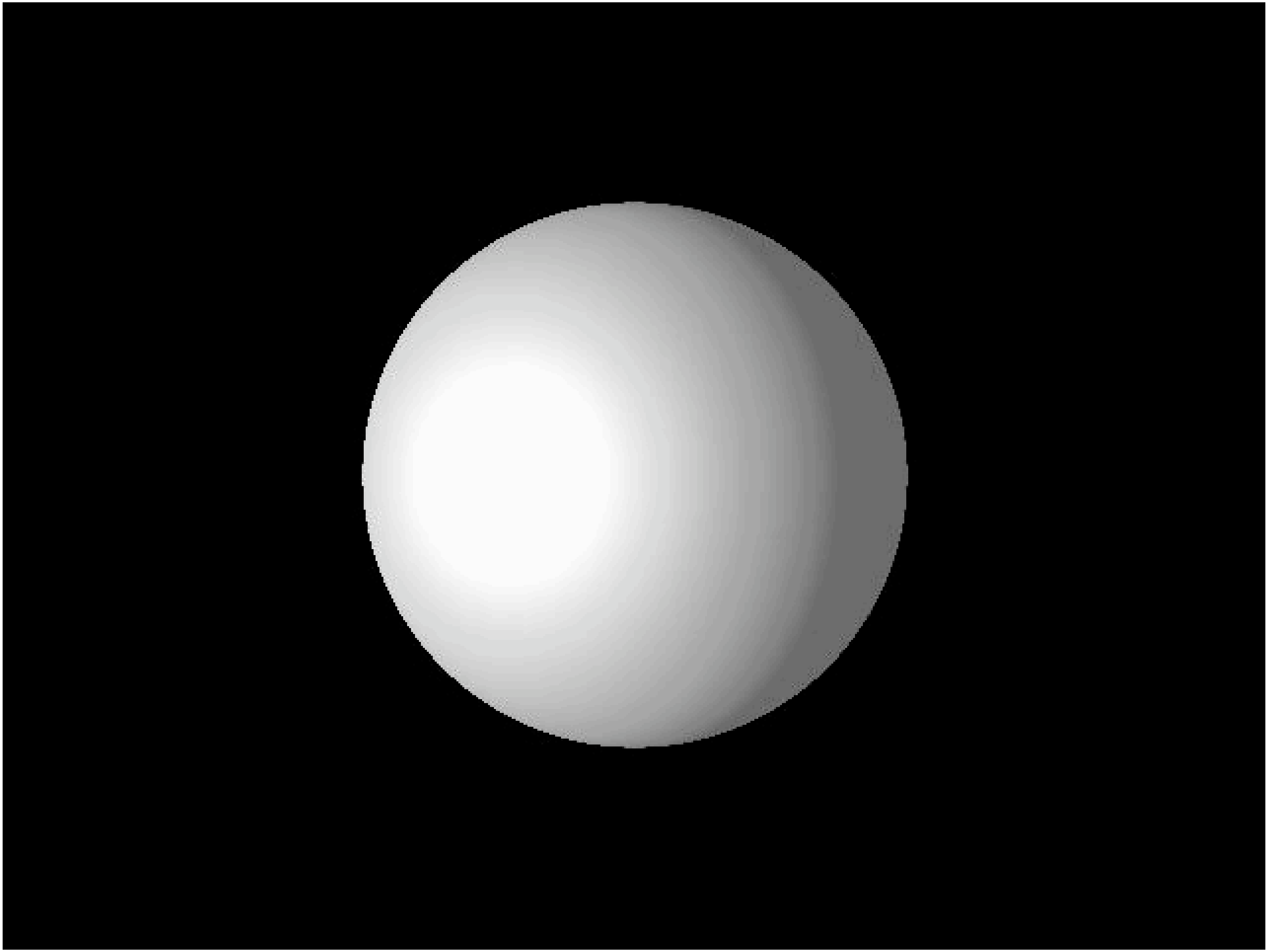
- Composites are affected by the shape and topology of their phases and the property contrast between phases
- Property contrast means, for example, E_2/E_1 (Young moduli ratio)
- If property contrast is small ($\leq$ 1-2), then composite properties do not depend much on shape of inclusions
- If property contrast is high (> 5-10), then composite properties do depend sensitively on shape of inclusions

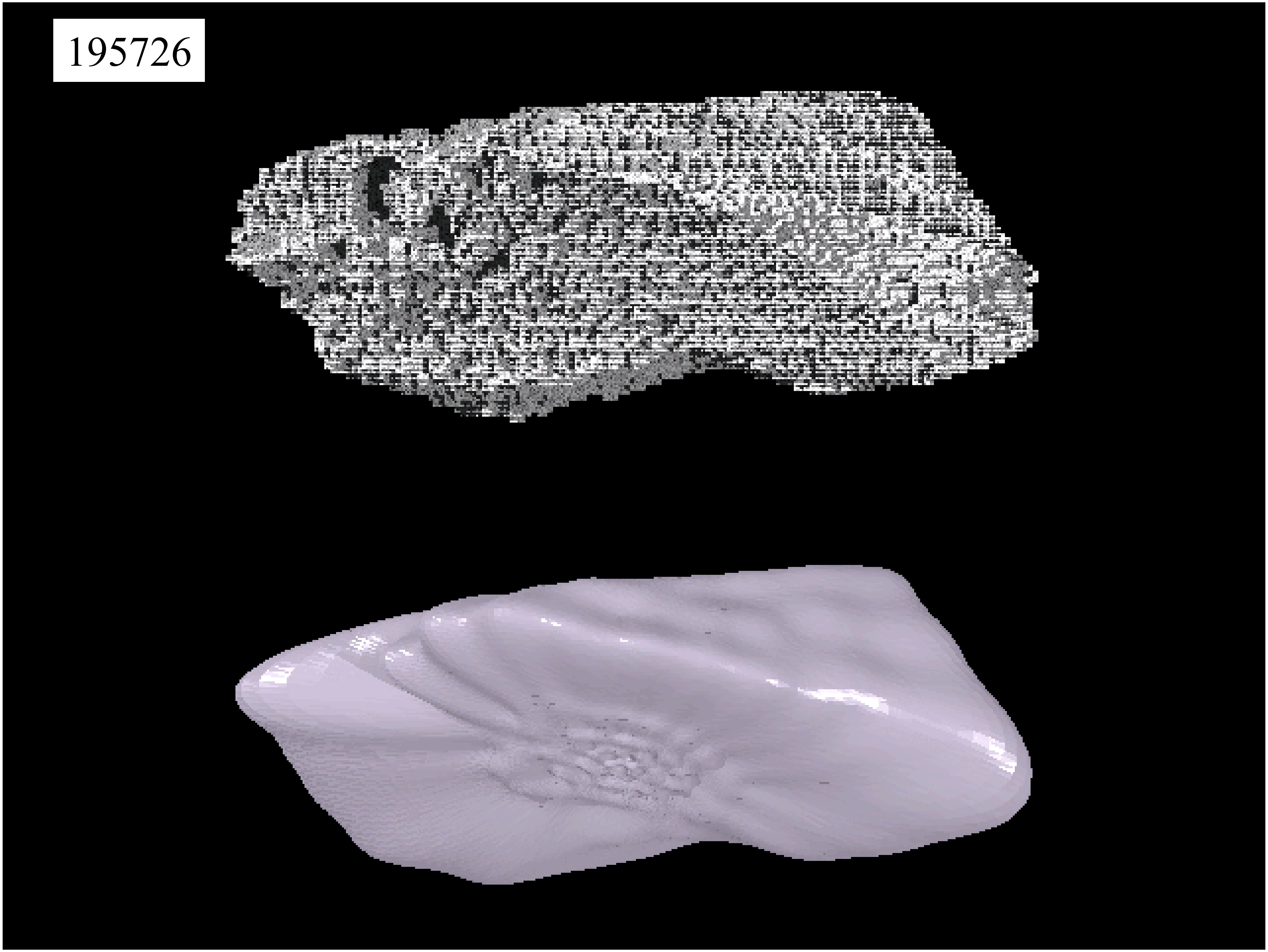
Concrete properties and aggregate shape

- Concrete is a composite = cement paste + aggregate, or mortar + coarse aggregate
- Diffusivity not affected much by aggregate shape at usual property contrast levels (~10%)
- Potential for elasticity to be affected quite a bit by aggregate shape (~50 % or more), especially at early ages, where elastic property contrast is high
- Potential for rheology to be greatly affected (~100%) by aggregate shape, since large property contrast
- So yes, it matters!

“Extract” aggregate shapes, then mathematically analyze and store them



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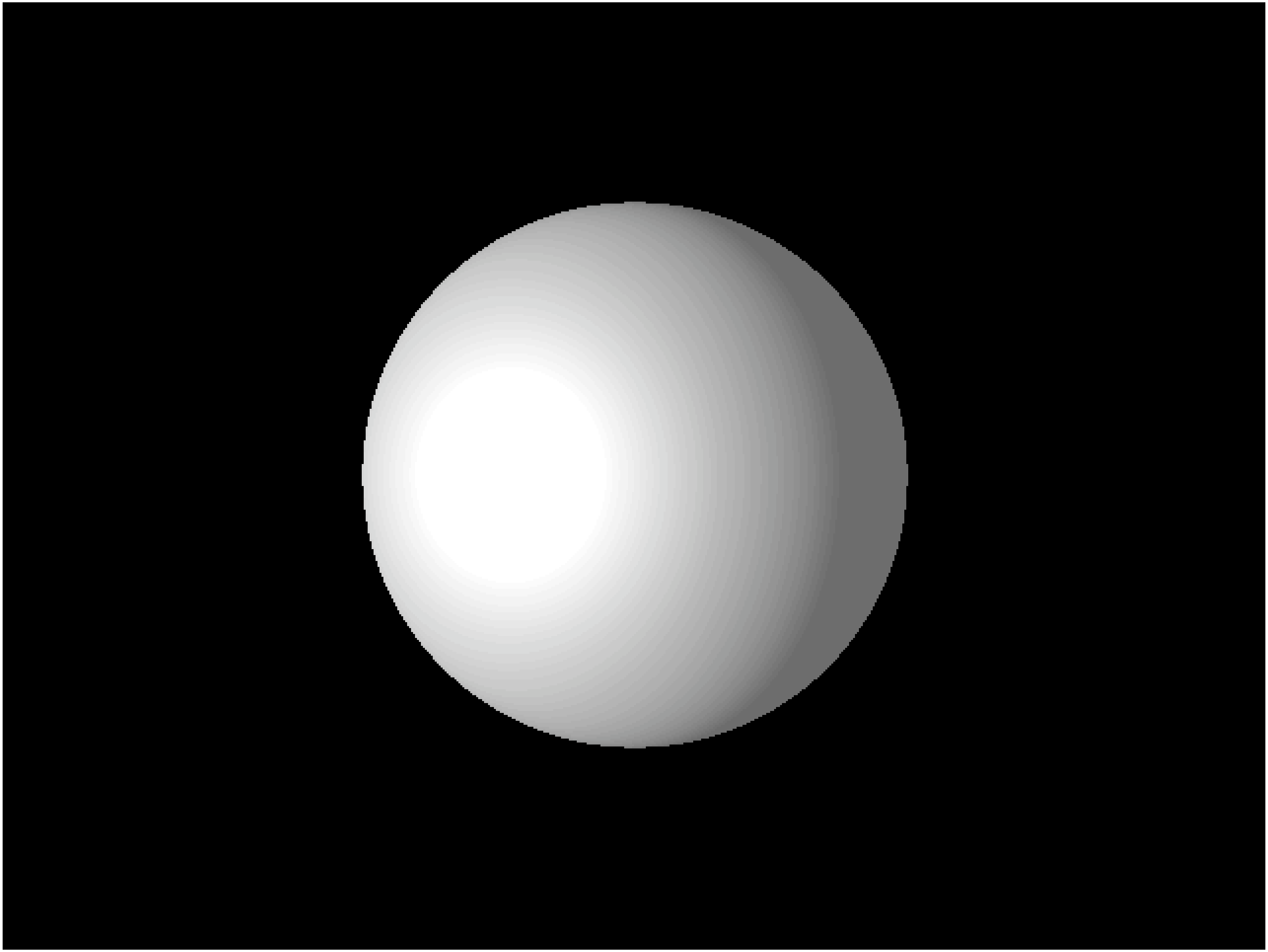
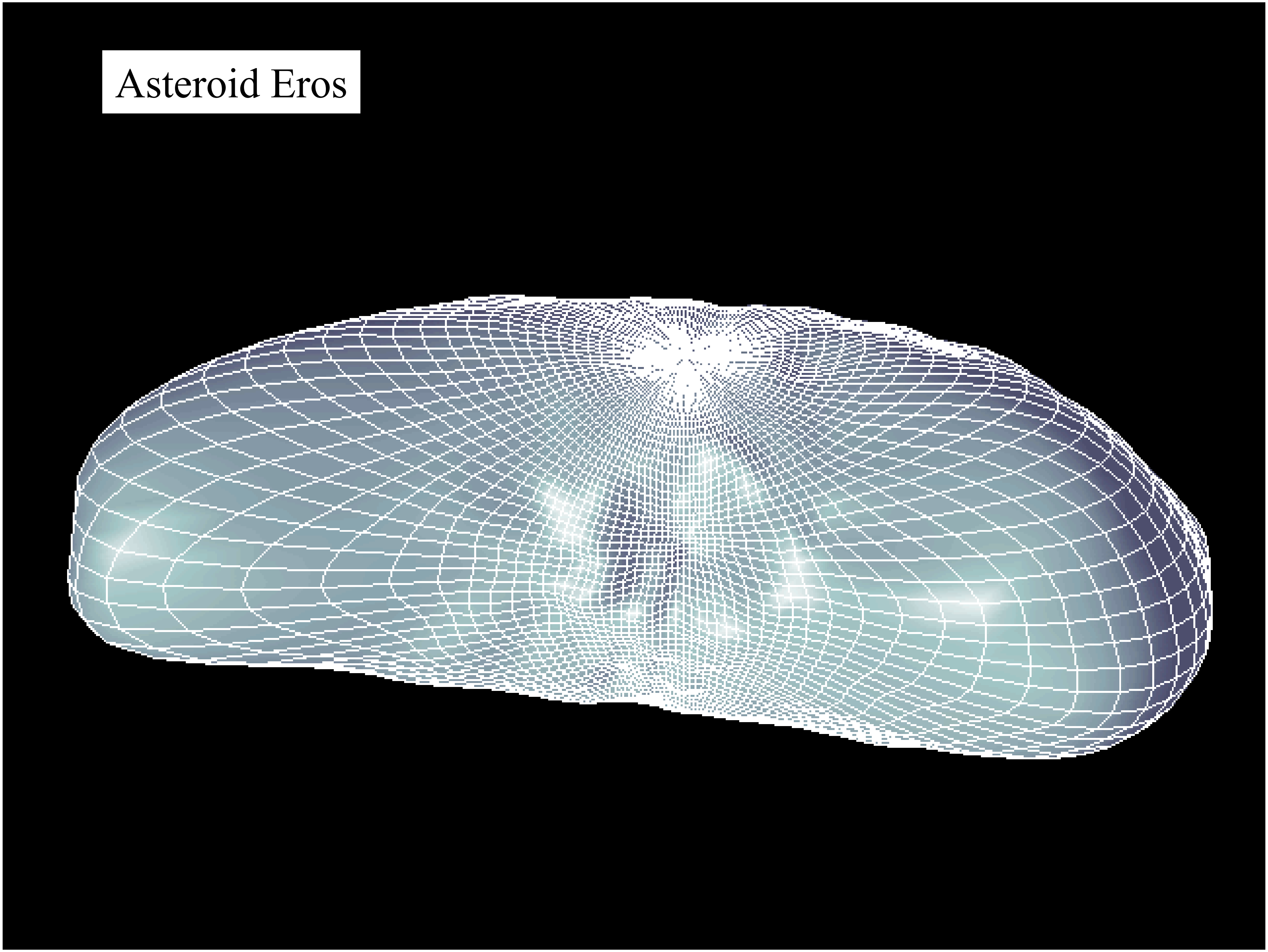


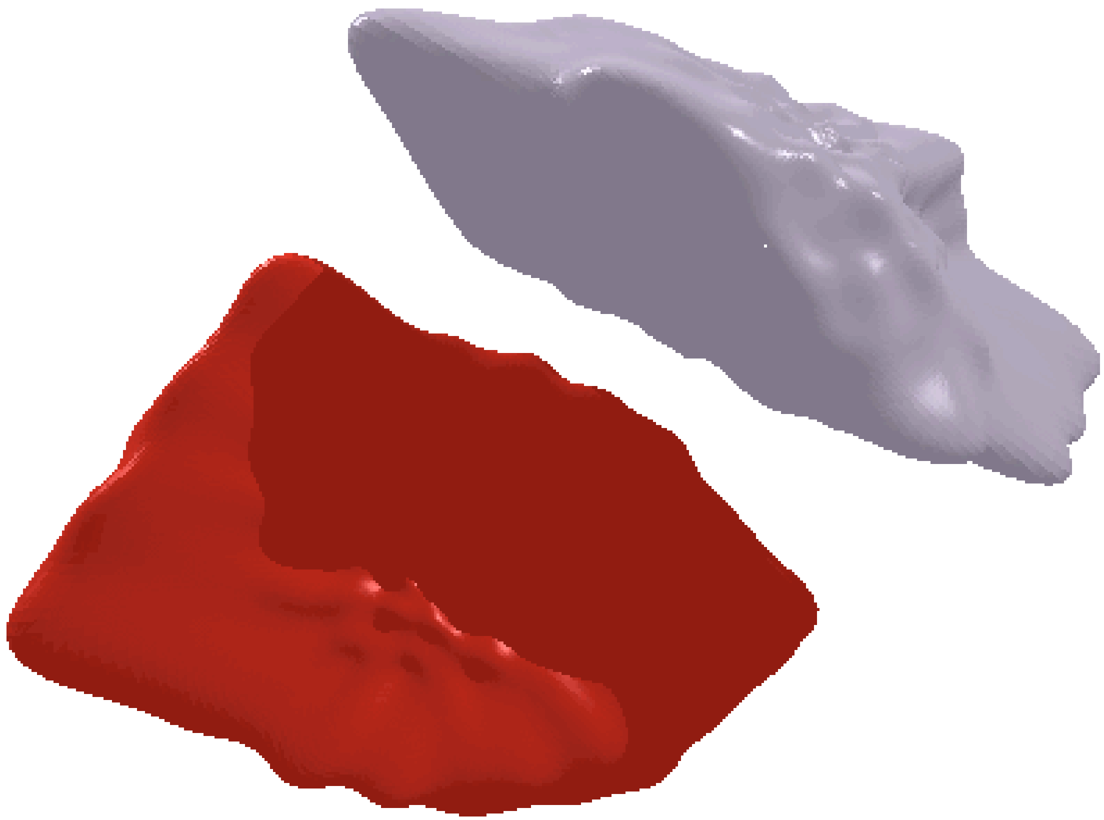

Asteroid Eros

ICAR/NIST collaboration

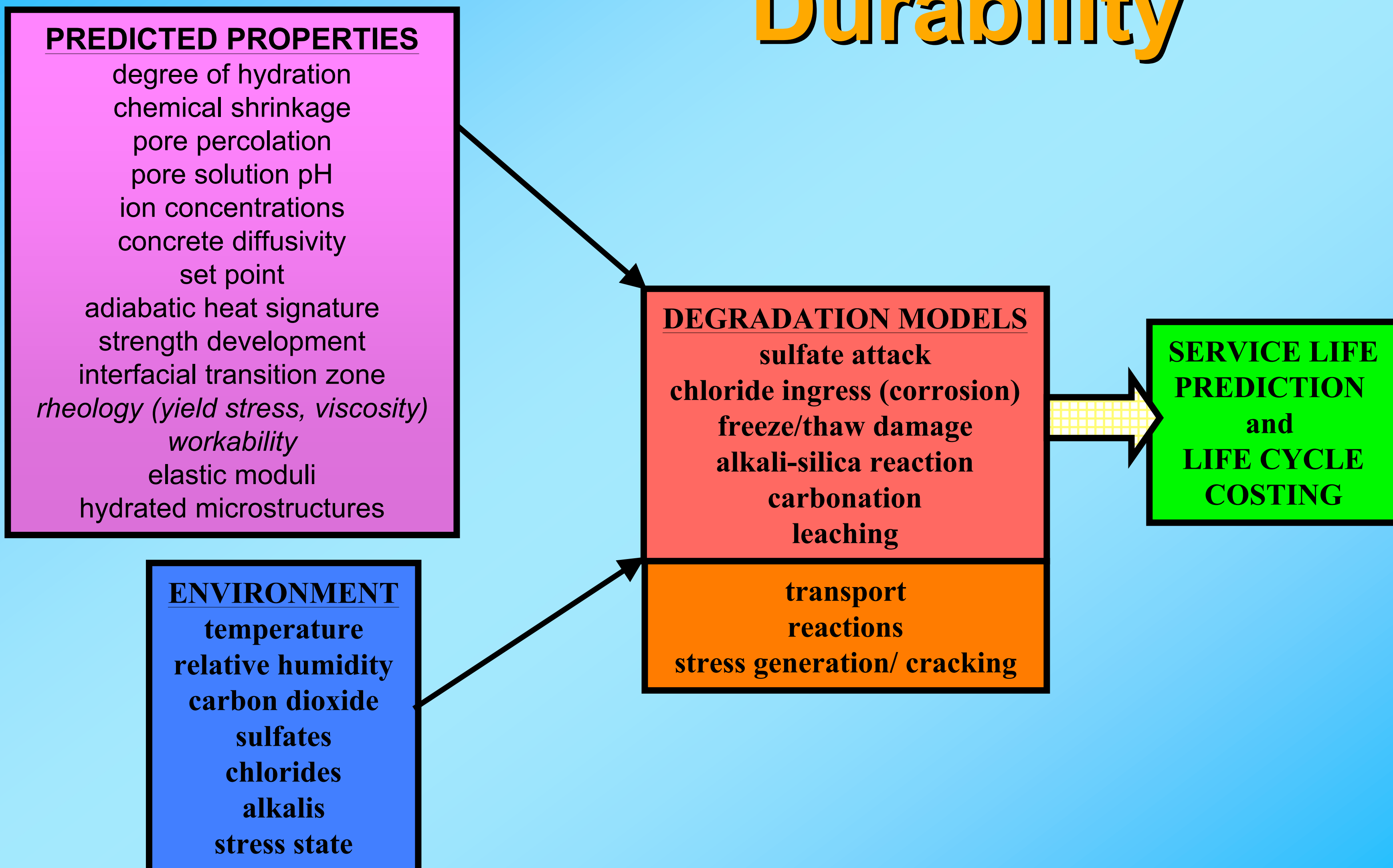
- UT-Austin supplies research collaboration requirement of VCCTL consortium membership - partnership between NIST and UT-Austin
- 2-way technology transfer, graduate students at NIST
- Build aggregate shape/properties/psd database, samples from ICAR members
- Statistical analysis of shape/psd information, relation of shape parameters to performance properties
- Quantitative addition of real-shape aggregates to models predicting elastic moduli, compressive strength, rheology/workability, and chloride penetrability

Requirements for Building Models with Particles

- When placing model particles in a model volume, need to:
  - Be able to tell if they overlap any existing particles
  - Place them at arbitrary positions and orientations
- Easy to do for spheres – just use center-center distance compared to sum of radii, no orientation
- Easy to do for any particle by eye/brain, hard for dumb computer to do
- Only possible for real-shaped particles by using spherical harmonic expansion



VCCTL Extension to Durability



Final Remarks

- VCCTL is based on years of computational and experimental materials science research
- VCCTL is being “made ready for prime time” with the help of companies and industrial groups
- These partners cover all the generic materials that make up concrete
- The field of cement and concrete materials needs to be, and will be, revolutionized
- VCCTL is leading the way
- Thanks to PCA for being one of the industrial groups that are helping to make VCCTL a reality